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Powder neutron diffraction study of the high temperature phase transitions in NaTaO₃

Brendan J Kennedy, A K Prodjosantoso and Christopher J Howard†

School of Chemistry, The University of Sydney, Sydney, NSW 2006, Australia

E-mail: b.kennedy@chem.usyd.edu.au, anti@chem.usyd.edu.au and
cjh@ansto.gov.au

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Abstract. Neutron powder diffraction has been used to examine the structural phase transitions in the perovskite-like NaTaO₃, from room temperature to 933 K. The room temperature orthorhombic structure (*Pbnm*, $a = 5.4768(1)$, $b = 5.5212(1)$, $c = 7.7890(2)$) transforms to orthorhombic *Cmcm* at around 700 K, then to tetragonal *P4/mbm* at 835 K, and finally to cubic *Pm $\bar{3}m$* above 890 K. The structure in orthorhombic *Cmcm* is characterized by simultaneous tilting of the oxygen atom octahedron about two of its tetrad axes, the tilting of successive octahedra being out of phase along the *b*-axis, and in phase along the *c*-axis. The two tilt angles are comparable just above 700 K, but the out-of-phase tilt angle falls smoothly to zero as the transition to tetragonal is approached, in the manner suggestive of a tricritical transition. This results in an unusual variation of lattice parameters with temperature in the orthorhombic *Cmcm* phase. In the tetragonal phase the lattice parameters vary smoothly; however near the transition to cubic the in-phase tilt angle changes more rapidly with temperature than might be expected in a continuous phase transition.

1. Introduction

As part of current systematic investigations of compounds of the perovskite family, with particular emphasis on the structural phase transitions [1–6], we have re-determined the crystal structures of NaTaO₃ and examined their evolution in the temperature range room temperature (300 K) to 933 K‡. The occurrence of three phase transitions in this temperature range has been well established, by optical microscopy [7, 8], differential thermal analysis [9] and powder diffraction techniques [10, 11]. From the first optical studies [7] it was suggested that the structure changed with increasing temperature from one orthorhombic structure to another orthorhombic to tetragonal and finally to cubic. Such a sequence was confirmed by neutron powder diffraction [11]. The temperatures reported for the three transitions [7–10] show some scatter: they range from 738 to 753 K for the first transition, and from 823 to 863 K and from 883 to 913 K for the two subsequent transitions. An early report [12] that NaTaO₃ was ferroelectric at room temperature has not been confirmed by more recent measurements [8, 9]. In the currently accepted (centrosymmetric) space group *Pbnm* for the room temperature structure [11, 13] NaTaO₃ could not be ferroelectric.

† On leave from Australian Nuclear Science and Technology Organisation, Private Mail Bag 1, Menai, NSW 2234, Australia.

‡ The authors became aware of the detailed neutron powder diffraction study of NaTaO₃ from about 750 K to 1000 K [25] only after this manuscript was submitted. There is gratifying agreement between the results from the present study and those from that earlier one.

Recently, within our own programme on perovskites, we have completed three detailed neutron powder diffraction studies [3, 4, 6] of the $I4/mcm$ tetragonal perovskite structure ($a^0a^0c^-$ in Glazer's notation [14]) as a function of temperature, and a similar study [5] of a perovskite with the $R\bar{3}c$ rhombohedral structure ($a^-a^-a^-$). NaTaO_3 was of interest because it provided an example of a perovskite transforming to the cubic phase from the alternative $P4/mbm$ tetragonal structure ($a^0a^0c^+$). Here we report a neutron powder diffraction study of NaTaO_3 to 933 K, in which we confirm the structures reported by Ahtee and Darlington [11], but provide more detail on the evolution of these structures with temperature.

2. Experimental procedure and data analysis

The NaTaO_3 was prepared by the solid state reaction of stoichiometric amounts of Na_2CO_3 (May and Baker 99.9%) and Ta_2O_5 (Aldrich 99.99%) at 700°, 800° and 900 °C in air for 24 hours at each temperature with re-grinding at every heating step. After a final re-grinding, the sample was annealed at 1150 °C for 48 h. As far as could be determined by x-ray powder diffraction the sample was single phase. For the neutron diffraction measurements, about 20 g of the powder was loaded into a thin-walled, 13 mm diameter, vanadium sample can, which was then placed in an ILL-type vacuum furnace. That furnace was mounted in turn on the neutron powder diffractometer on beam port HB4 at the High Flux Isotope Reactor, Oak Ridge National Laboratory [15]. Diffraction patterns were recorded, using neutrons of wavelength 1.500 Å, over the 2θ range from 11 to 135°, with a step size of 0.05°. Patterns were collected first at room temperature and then at successively higher temperatures, to a maximum of 933 K. The furnace was pumped throughout the experiment, maintaining a vacuum of about 10^{-6} Torr. The crystal structures were refined by the Rietveld method, using program LHPM [16] operating on a PC. The background was taken to be a quadratic function of 2θ , and was refined simultaneously with the unit-cell, zero-point, scale, peak width/shape/asymmetry and crystal structure parameters. The peak profile was described by a Voigt function, in which the widths of the Gaussian and Lorentzian components were coded to vary in accordance with the Caglioti–Paoletti–Ricci function [17] to describe instrumental resolution and strain broadening, and with $\sec\theta$ to describe crystallite size broadening, respectively. The 2θ region near 38° affected by a peak from the Nb furnace heating element was excluded from the refinements.

3. Results and discussion

Neutron powder diffraction patterns were recorded at 16 temperatures from room temperature to 933 K inclusive. From inspection and analysis of these diffraction patterns we concluded that the structures that form on increasing temperature are orthorhombic $Pbnm$, orthorhombic $Cmcm$, tetragonal $P4/mbm$ existing over a limited temperature range from about 835 to 890 K, and finally cubic $Pm\bar{3}m$. Diffraction patterns representative of these different phases are shown (over a selected angle range) in figure 1—this figure serves to illustrate some of the weak reflections that are diagnostic of the different phases. The temperature variations of the reduced cell parameters and primitive cell volume are shown in figure 2.

3.1. The room temperature orthorhombic structure

In the first attempt on the crystal structure of NaTaO_3 [18] the space group was claimed to be (noncentrosymmetric) $Pc2_1n$, consistent with the early report [12] of ferroelectric behaviour of the compound. Though x-ray single crystal methods were used, the data were sparse, and

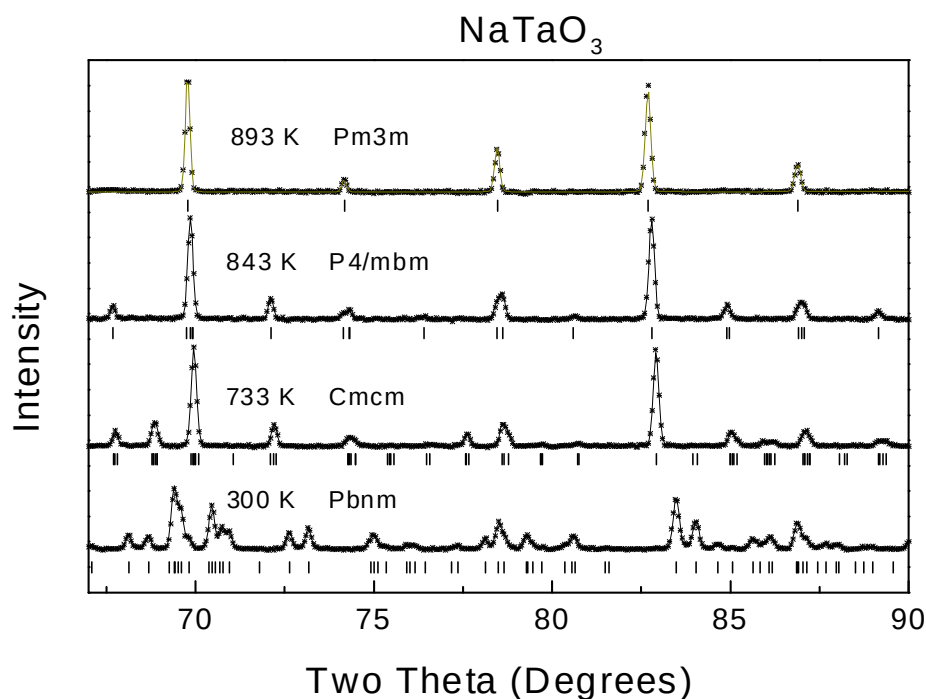


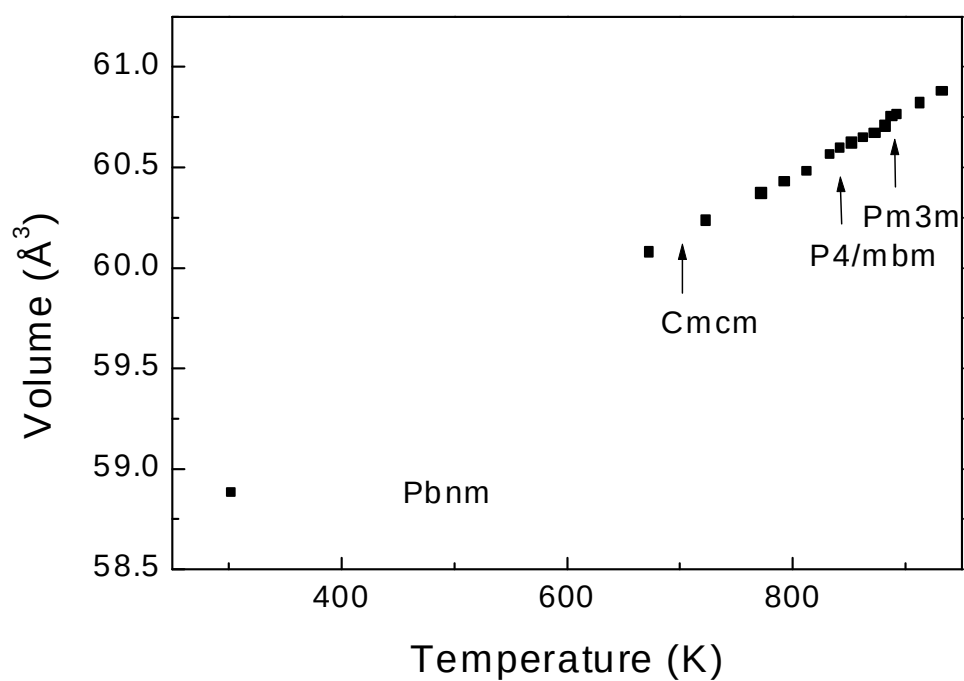
Figure 1. Part of the powder neutron diffraction profiles ($\lambda = 1.500 \text{ \AA}$) from NaTaO₃ at selected temperatures with the results of fitting by the Rietveld method. The crosses are the observed data and the solid lines the calculated patterns. Positions of Bragg reflections for each temperature are marked. The measures of fit are, at 300 K R_p 7.63, R_{wp} 9.62 (R_{exp} 8.59) R_{Bragg} 2.44; at 733 K R_p 7.05, R_{wp} 8.85 (R_{exp} 8.54) R_{Bragg} 1.77; at 843 K R_p 7.25, R_{wp} 9.02 (R_{exp} 8.55) R_{Bragg} 2.02; and at 893 K R_p 7.81, R_{wp} 9.65 (R_{exp} 8.57) R_{Bragg} 1.35.

the space group determination not entirely convincing. Ahtee and Unonius [13] argued from x-ray powder diffraction data that the space group was the commonly observed *Pbnm*, and Ahtee and Darlington [11] confirmed this result from neutron powder diffraction. More recent dielectric measurements [8, 9] are consistent with this conclusion.

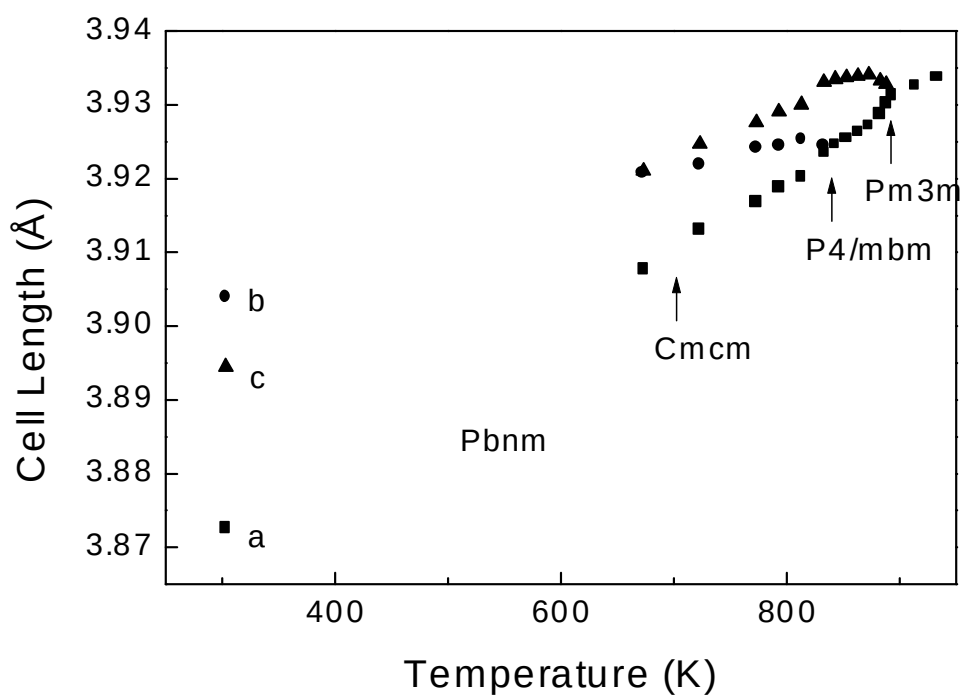
The pattern recorded at room temperature was fitted, therefore, assuming a structure in *Pbnm*. The excellent fit together with well resolved splitting of the 404–044 pair at just under 84° confirms the space group choice [4]. The pattern and fit are shown in figure 1, and the corresponding crystal structure parameters are recorded in table 1. The lattice parameters are in good agreement with those from the previous neutron study [11]. The co-ordinates included in table 1 have been chosen to conform with those shown in previous studies of perovskites in *Pbnm* [1, 3, 4, 6, 19]. These co-ordinates can not be compared directly with those given by Ahtee and Darlington, who used *Pcmn* [11]; however after the appropriate transformation† the refined structures are in good agreement.

The orthorhombic perovskite in *Pbnm* involves the tilting of TiO₆ octahedra, in-phase tilting of octahedra about the *c*-axis and tilting about those diad axes of the octahedra (approximately) parallel to the *b*-axis. As explained in a previous contribution [4], it is possible

† We can fit our pattern in *Pcmn*, with $a = 5.4768$, $b = 7.7890$, $c = 5.5212 \text{ \AA}$ and with Ta at $(1/2, 0, 0)$, Na at $(-0.0023, 1/4, -0.0180)$, O1 at $(1/2 - 0.0616, 1/4, 0.0101)$ and O2 at $(1/4 + 0.0357, -0.0310, 1/4 + 0.0345)$.



(a)



(b)

Figure 2. Temperature dependence of (a) the volume of the primitive cell and (b) the reduced lattice parameters for NaTaO₃.

Table 1. Structures and structural parameters for NaTaO₃ at selected temperatures.

Atom	Site	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> (Å ²)
300 K <i>Pbnm</i> <i>a</i> = 5.4768(1), <i>b</i> = 5.5212(1), <i>c</i> = 7.7890(2) Å					
Na	4c	0.0023(8)	0.5180(9)	1/4	1.1(2)
Ta	4a	0	0	0	0.3(1)
O1	4c	−0.0616(4)	−0.0101(5)	1/4	0.6(1)
O2	8d	0.2143(3)	0.2845(3)	0.0310(2)	0.6(1)
773 K <i>Cmcm</i> <i>a</i> = 7.8337(2), <i>b</i> = 7.8485(3), <i>c</i> = 7.8552(3) Å					
Na1	4c	0	0.0021(40)	1/4	4.2(9)
Na2	4c	0	0.4942(31)	1/4	2.6(6)
Ta	8d	1/4	1/4	0	0.7(2)
O1	8e	0.2738(9)	0	0	2.2(3)
O2	8f	0	0.2229(9)	0.0214(9)	1.7(2)
O3	8g	0.2750(9)	0.2500(13)	1/4	2.6(3)
843 K <i>P4/mbm</i> <i>a</i> = <i>b</i> = 5.5503(1), <i>c</i> = 3.9335(1) Å					
Na	2c	0	1/2	1/2	3.4(2)
Ta	2a	0	0	0	0.7(1)
O1	2b	0	0	1/2	3.1(1)
O2	2b	0.2741(3)	0.7741(3)	0	2.4(1)
893 K <i>Pm</i>$\bar{3}$<i>m</i> <i>a</i> = <i>b</i> = <i>c</i> = 3.9313(1) Å					
Na	1b	1/2	1/2	1/2	3.6(1)
Ta	1a	0	0	0	0.8(1)
O	3d	1/2	0	0	3.1(1)

to make estimates of these tilt angles from the lattice parameters† assuming *rigid* octahedra, or preferably from the oxygen atom co-ordinates themselves. The results for angles of tilt around the diad axis and the *c*-axis estimated from oxygen co-ordinates (lattice parameters) are 9.9 (7.3) and 8.0° (6.1°) respectively.

In the pattern recorded at 673 K, the superlattice reflections together with the splitting of the 404–044 pair showed that the space group was still *Pbnm*. At this temperature the angles of tilt around the diad axis and the *c*-axis as estimated from oxygen co-ordinates (lattice parameters) are 6.7 (4.7) and 6.4° (4.7°) respectively. The equality of the tilt angles estimated from the lattice parameters simply reflects the fact that reduced lattice parameters $b/\sqrt{2}$ and $c/2$ are almost equal.

3.2. The higher temperature orthorhombic structure

In the pattern recorded at 723 K, there was no sign of the *Pbnm* characteristic peak splitting seen at lower temperatures, and indeed a structural model in space group *Cmcm* provided a better fit to the observed pattern than one in *Pbnm*. Consequently all patterns recorded in the temperature range 723 to 813 K were refined in space group *Cmcm*. The pattern recorded at 773 K and the fit obtained are displayed (in part) in figure 1, and the corresponding parameters are recorded in table 1. The structure is as determined by Ahtee and Darlington [11].

The tilt system in *Cmcm* (at least with the present choice of co-ordinates) comprises out-of-phase tilting of the oxygen octahedra around the *b*-axis and in-phase tilting around the *c*-axis. This is denoted in Glazer's notation [14] as $a^0b^-c^+$. In line with our previous practice [2–4, 6]

† There is an error in [4]—expressions for $\cos \psi$ and $\cos \varphi$ given on p 1485 of that reference should be interchanged.

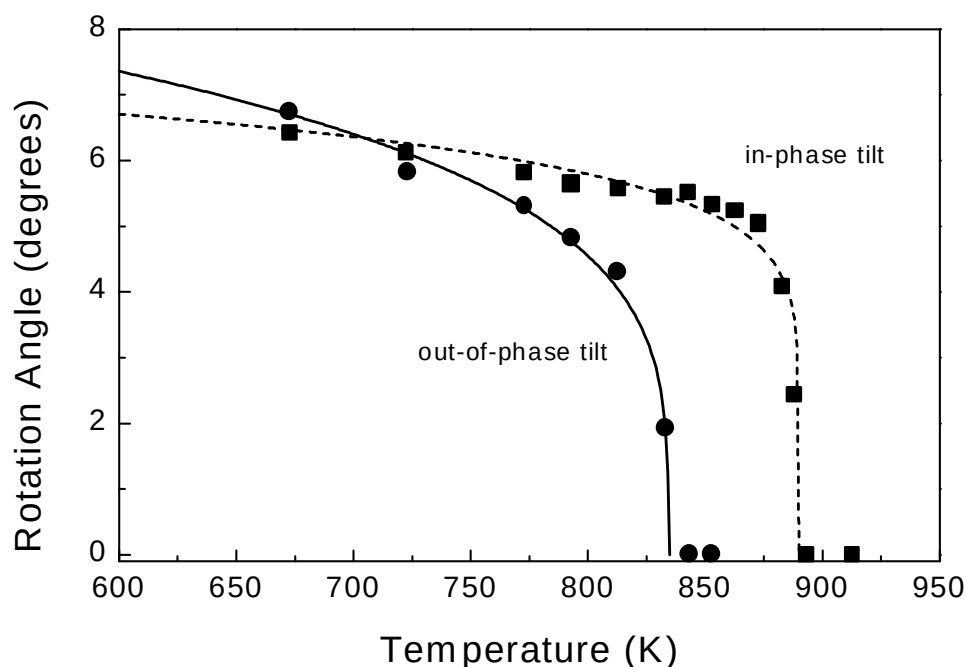


Figure 3. Temperature dependence of the octahedral tilt angles for NaTaO₃. The solid line through the out-of-phase tilts is calculated with $\varphi = A(T_i - T)^{1/4}$ where $A = 1.88$ and $T_i = 834.2$ K and the dashed line through the in-phase tilts is calculated with $\psi = B(T_c - T)^{1/8}$ where $B = 3.30$ and $T_c = 890$ K.

we denote the rotation angles for the in-phase and out-of-phase tilting by ψ and φ respectively. Were the octahedra to remain rigid, it would be possible to calculate these rotation angles from the lattice parameters. Specifically, the rotation around the b -axis would reduce the values of a and c by the factor $\cos \varphi$ while the rotation around† the c -axis would reduce the values of a and b by the factor $\cos \psi$. The values of ψ and φ would be given by $\cos \varphi = a/b$ and $\cos \psi = a/c$ in this case. Since the octahedra are generally not rigid, it is preferable to estimate the tilt angles from the oxygen atom co-ordinates according to formulae given previously [4]. At 773 K the angles of tilt around the b -axis and the c -axis as estimated from oxygen co-ordinates (lattice parameters) are 5.3 (3.5) and 5.8° (4.2°) respectively. The temperature dependence of the tilt angles estimated from the oxygen co-ordinates is shown in figure 3.

3.3. Tetragonal structure

Patterns recorded at sample temperatures from 843 to 888 K inclusive showed weak superlattice lines corresponding to the tetragonal structure with in-phase tilting ($a^0a^0c^+$), in space group $P4/mbm$. Refinements based on this structure were successful, with appreciably better agreement between observed and calculated profiles being obtained when anisotropic displacement parameters were employed. The pattern recorded at 843 K and the fit obtained are displayed (in part) in figure 1, and the corresponding parameters are recorded in table 1. The structure is again as reported by Ahtee and Darlington [11].

† The results are only approximate when the tilts are applied simultaneously.

In the $P4/mbm$ tetragonal structure the O2 atom is at $(1/4 + u, 3/4 + u, 0)$ and the angle of the in-phase rotation is given by $\tan \psi = 4u$. This angle is 5.5° at 843 K and diminishes with increasing temperature as shown in figure 3.

At 843 K the NaO₆ octahedra are slightly tetragonally compressed with the axial Na–O1 bonds being about 0.005 Å shorter than the basal Na–O2 bonds, 1.9668(1) versus 1.971(2) Å. It is interesting to recall that in our previous measurements on tetragonal perovskites, specifically on SrRuO₃ [1], SrZrO₃ [3], SrHfO₃ [6] and CaTiO₃ [4] we also found the octahedra were to some degree tetragonally compressed. Recently, Darlington suggested from the lattice parameter variation (figure 1(b) in [20]) that the octahedra in tetragonal $I4/mcm$ and $P4/mbm$ perovskites are invariably elongated along the octahedral rotation axis.† We see a similar variation of lattice parameters with temperature (in our figure 2) but find that the octahedra are slightly compressed along this axis. Darlington notes a fall in the a -parameter below the cubic to tetragonal phase transition which he identifies as the full effect of octahedral rotation, then interprets a concomitant rise in the c -parameter as elongation of the octahedron. In fact the reduction in the a -parameter is rather less (that is the a -parameter remains larger) than the measured octahedral rotation would imply, and in consequence the octahedra expand perpendicular to the rotation axis. In effect the octahedra become tetragonally compressed. The rise in the c -parameter below the transition point is probably driven by a tendency of the octahedra to approach regularity, but as is observed they do remain slightly tetragonally compressed in the tetragonal phases. It is evidently a weakness of Darlington's argument that it makes no reference to measured oxygen co-ordinates nor to the octahedral rotation angles that can be derived from them.

As mentioned above, better results were obtained using anisotropic displacement parameters. The atomic displacements of the sodium and tantalum atoms were nearly isotropic, but the mean square displacements of the oxygen atoms perpendicular to the Ta–O bonds were approximately four times those along the bonds. Similar anisotropy has been noted in studies of other tetragonal perovskites [1–4, 6]. We show the equivalent isotropic displacement parameters in table 1.

3.4. Cubic structure

The diffraction patterns recorded at 893 K and above do not contain superlattice peaks (see figure 1), and are fitted assuming the ideal cubic perovskite, in space group $Pm\bar{3}m$, the co-ordinates being listed in table 1. The atomic displacements of the oxygen atoms show significant anisotropy, the largest displacement amplitudes being observed perpendicular to the Ta–O bonds.

4. Phase transitions

It is evident from our study that the high temperature phase transitions in NaNO₃ occur in the following sequence:

$$Pbnm \xleftrightarrow[720\text{ K}]{} Cmcm \xleftrightarrow[835\text{ K}]{} P4/mbm \xleftrightarrow[809\text{ K}]{} Pm\bar{3}m.$$

Our results agree with previous results [7–10] in so far as we find three transitions above room temperature, and the symmetries involved (orthorhombic to orthorhombic to tetragonal to cubic) are as proposed by Cross [7]. The space group assignments made by Ahtee and Darlington [11] from their neutron diffraction study are confirmed. The sequence of structures is as previously reported for SrZrO₃ [3, 21] and SrHfO₃ [6], and suggested for CaTiO₃ [4],

† The recently published analysis by Darlington and Knight [25] is correct. Indeed these authors note that the metal-oxygen bonds perpendicular to the rotation axis lengthen by about 0.001 Å per degree of tilt.

except for the fact that in the tetragonal phase $P4/mbm$ has replaced $I4/mcm$. It can be seen from the work of Howard and Stokes [2] that transitions from orthorhombic $Cmcm$ to the cubic $Pm\bar{3}m$ can proceed continuously through either of these intermediate tetragonal phases. The temperature found for the first transition is lower than previously reported. This is thought to be due to problems of temperature calibration, probably related to the operation of the high temperature ILL furnace below its normal range. The temperatures for the second and third transitions fall within the ranges previously reported.

There is little reason to doubt that the structure of NaTaO_3 at room temperature is the $Pbnm$ orthorhombic structure, which is the most commonly occurring structure in the perovskite family [22, 23]. The structure shows octahedral tilting simultaneously around a tetrad and a diad axis of the octahedron, and we estimate the tilt angles as 8.0 and 9.9 respectively. The transition from $Pbnm$ ($a^-a^-c^+$) to $Cmcm$ ($a^0b^-c^+$) cannot, for reasons given previously [2, 3], be continuous. The transition is a subtle one nonetheless. It is interesting to note that the tilt angles become nearly equal, 6.4 and 6.7, and the reduced cell becomes almost tetragonal ($c/2 \approx b/\sqrt{2}$), near the onset of the transition to $Cmcm$.

The structure in $Cmcm$ just after the transition has in-phase octahedral tilts around the c -axis and out-of-phase tilts around the b -axis that are nearly equal, 5.8 and 5.3°. The transition from $Cmcm$ ($a^0b^-c^+$) to $P4/mbm$ ($a^0a^0c^+$) can be continuous [2] if the out-of-phase tilt angle diminishes continuously towards zero as the temperature is raised. The tilt angles are shown in figure 3 where it can be seen that the in-phase tilt decreases only slightly over the temperature range of the $Cmcm$ phase while the out-of-phase tilt angle diminishes continuously to zero. It is possible to reproduce this diminution of the out-of-phase tilt angle using the expression $\varphi \propto (T_t - T)^{1/4}$ where T_t is the temperature of the transition to the tetragonal phase. Such behaviour is encountered in tricritical phase transitions [24]. The behaviour of the lattice parameters through the $Cmcm$ phase can be understood, at least qualitatively, by referring to the relations between these parameters and tilt angles given in section 3.2. Near the lower temperature boundary of the $Cmcm$ phase the tilt angles are roughly equal, making a shorter than b and c , and the last two roughly equal. As the temperature increases, φ but not ψ approaches zero, bringing a and b closer together, but leaving both shorter than c . This is indeed what is observed. A more quantitative treatment is not warranted since, as we have noted earlier, octahedral distortions render relationships between tilt angles and lattice parameters only approximate.

The transformation from the tetragonal structure $P4/mbm$ ($a^0a^0c^+$) to cubic ($a^0a^0a^0$) can also be continuous in Landau theory [2]. It involves only the single octahedral tilt angle, ψ . This angle (figure 3) varies continuously through the transition from orthorhombic into the tetragonal phase, then diminishes apparently continuously to zero as the transition to cubic is approached. In the same temperature region the lattice parameters also vary smoothly. However the rotation angle itself approaches zero rather too rapidly. Its temperature variation is better described by $\psi \propto (T_c - T)^{1/8}$ where T_c is the temperature of the transition to the cubic phase, than by a function involving the exponent 1/2 as would be expected for a second order or 1/4 for a tricritical transition. This rapid decrease is not yet understood, and for this reason the possibility that the transition is first order cannot yet be ruled out.

Acknowledgments

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