

Lattice Parameters and Tilted Octahedra in Sodium–Potassium Niobate Solid Solutions

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Measurements of lattice parameters and intensities of difference reflexions have been made for all compositions of $\text{Na}_{1-x}\text{K}_x\text{NbO}_3$, both at room temperature and above. Structural models are proposed for each phase found.

1. Introduction

Since the dielectric properties of NaNbO_3 were reported (Matthias, 1949) it and related materials have been under extensive study. The perovskite sodium–potassium niobate system is of interest because it shows a number of ferroelectric phases with high spontaneous polarization. They are also attractive for their piezoelectric applications. Sodium–potassium niobate ceramics are, for example, used in delay-line transducers because of their relatively low dielectric constants and high electromechanical coupling coefficients (Egerton & Dillon, 1959). For industrial applications the control of properties of the material is of the utmost importance in order to obtain materials having a required value of a particular property at room temperature. This control of properties often becomes possible by varying the constituents in solid solutions. The ultimate purpose of the present work is therefore to find relationships between the physical properties and the structure of the material. This work is also a continuation of earlier structural work on NaNbO_3 (see for example, Ahtee, Glazer & Megaw, 1972; Glazer & Megaw, 1972, 1973), which has proved a very useful material in this context because its ideal structure is so simple and yet the possible departures from it so various.

In Fig. 1, the phase diagram of the sodium–potassium niobate system is drawn with the most recent data and some preliminary interpretations (Ahtee & Glazer, 1974). In addition, we have altered the phase diagram to take into account more recent results which will be reported here (and also by Ahtee & Glazer, 1975). For convenience we have labelled the different phase fields with capital letters.

Shirane, Newnham & Pepinsky (1954) have reported dielectric measurements on the mixed $\text{Na}_{1-x}\text{K}_x\text{NbO}_3$ ceramics. They observed well-defined ferroelectric hysteresis loops from room temperature up to about 400°C for compositions from about 10 to 100 mole % K. At about 200°C there was a transition point at all compositions. The phases above 400°C were found to be

paraelectric. In addition Cross (1958) has examined optically the region 0–10 mole % K. The left-hand side of Fig. 1 is based mainly on his work together with the most recent results for NaNbO_3 . Substitution of more than 0.6 mole % K for Na in NaNbO_3 introduces the same ferroelectric phase as found in pure NaNbO_3 at high fields – the forced ferroelectric phase, *Q* (Megaw & Wells, 1958). Cross (1956) has also predicted theoretically the KNbO_3 – NaNbO_3 phase diagram from phenomenological arguments, and Darlington (1975) has discussed this in greater detail using the results reported by us earlier. Wood, Miller & Remeika (1962) argued from the plot of lattice parameters *versus* composition given by Shirane, Newnham & Pepinsky (1954) that the phase boundary must lie close to 35 mole % K. This was supported by the observation of extra X-ray diffraction lines found by Reisman & Banks (1958).

The thermal and X-ray diffraction measurements of Tennery & Hang (1968) have revealed how complicated the sodium–potassium niobate system really is. They found the presence of phase boundaries at 17.5, 32.5 and 47.5 mole % K at room temperature in addition to those reported by Cross. They observed that in the

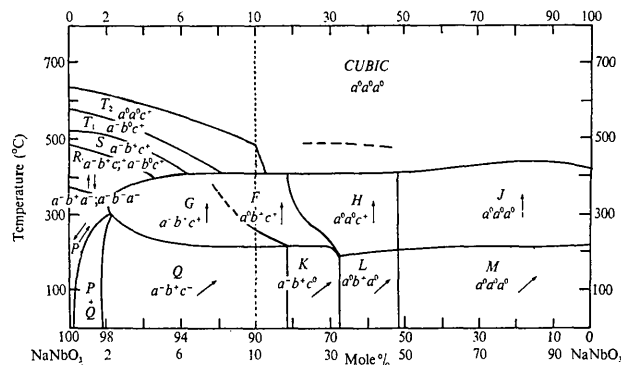


Fig. 1. Phase diagram of $\text{Na}_{1-x}\text{K}_x\text{NbO}_3$. The phase fields have been determined from past and present work. Vertical arrows indicate one-corner displacements and inclined arrows indicate two-corner displacements. In each phase the tilt system is indicated according to the scheme of Glazer.

region $0.02 < x < 0.175$ there were three difference (or superlattice) lines with $N = h^2 + k^2 + l^2 = 2\frac{1}{2}, 2\frac{3}{4}, 3\frac{1}{2}$, when indexed on the pseudocubic subcell. For $0.175 < x < 0.325$ the reflexion with $N = 2\frac{3}{4}$ was not observed, and no difference reflexions at all were found at any other compositions.

From the structural point of view, in ABO_3 perovskites there are three main features to be recognized (Megaw, 1971). Firstly, the corner-linked O octahedra are usually only distorted to a minor extent, so that to a first approximation, we can treat them as rigid units. Secondly, off-centring of B cations inside the octahedra can occur, which is associated with the phenomenon of ferro- or antiferro-electricity. The sense of the displacement in one octahedron influences that in the next through the polarization of the common octahedron corners consisting of O atoms; one-corner displacements of the B-cations give chain dipoles, two-corner give sheet dipoles and three-corner a single three-dimensional dipole (Megaw, 1969). Thirdly, the octahedra may tilt in a variety of configurations and have a considerable effect on the lattice parameters. Structures with tilted octahedra show abnormal elasticities whether or not dipole moments are present, and also have larger mean linear expansions than structures in which the orientation of the octahedra is fixed by symmetry. The arrangement of tilted octahedra also determines the sense of adjacent chains or sheets. Furthermore, reversal of small off-centre displacements is easier if they are not coupled by symmetry to the sense of tilt (Megaw, 1971). The tilting can be described by three component tilts taken about the three tetrad axes of the octahedra (Glazer, 1972a) (on the phase diagram, the tilt systems in each phase are marked using Glazer's classification scheme). The tilting of the octahedra causes doubling of the unit-cell axes perpendicular to the tilt axes and gives rise to difference reflexions corresponding to half-integral reciprocal-lattice layers. In fact, from the lattice parameters and the indices of certain difference reflexions we can derive trial models of the structures (Glazer, 1972a, 1975; Glazer & Ishida, 1974).

From the tilt-system classification it can be seen that there are essentially two kinds of tilt, in-phase tilts (+), where the successive octahedra along a pseudocubic axis are tilted in phase about this axis, and corresponding antiphase tilts (-). The + tilts give rise to differ-

ence reflexions with indices euu , ueu and uue , where e and u mean integral and half-integral indices respectively (even and odd indices with respect to the true, doubled unit-cell). On the other hand, - tilts produce reflexions with indices uuu . If the angles of tilt about [100], [010] and [001] are denoted by α , β and γ respectively, the intensities of the difference reflexions corresponding to the tilt angles have the following relations (Glazer & Ishida, 1974; Glazer, 1975). For + tilts

$$\begin{aligned} I(euu) &\propto (ki^l - li^k)^2 \alpha^2 \\ I(ueu) &\propto (-li^h + hi^l)^2 \beta^2 \\ I(uue) &\propto (hi^k - ki^h)^2 \gamma^2. \end{aligned} \quad (1)$$

For - tilts

$$I(uuu) \propto [(ki^l - li^k)\alpha \pm (-li^h + hi^l)\beta \pm (hi^k - ki^h)\gamma]^2 \quad (2)$$

where the \pm signs depend on the particular choice of origin for the tilt system, and $i = \sqrt{-1}$.

The purpose of this paper is to derive from the accurate measurements of lattice parameters and difference reflexions the possible space groups of the different phases of $Na_{1-x}K_xNbO_3$ solid solutions. To obtain a more detailed picture of what is really happening in the structural changes a complete set of data has to be collected for the determination of the magnitudes and directions of the atomic displacements. Since the growth of single crystals at all compositions is difficult, this is most conveniently done by the profile refinement technique (Rietveld, 1969; Hewat, 1973). However, the profile refinement method is a technique for structure refinement and not structure determination. For this method we need first of all a suitable starting model comprising an approximate estimate of where the atoms are in the unit cell and also the correct space group.

In order to find the space groups we collected data for the accurate determination of the lattice parameters and the intensities of the difference reflexions so that the above-mentioned principles could be applied. The information gleaned from the lattice parameter determinations, both from single crystals and polycrystalline samples, is collected in § 3 and that from the difference reflexions in § 4. Finally, in § 5 we have summarized the results for each phase in turn. Unless otherwise specified we refer all axes to the pseudocubic subcell.

Table 1. Summary of compositions and room-temperature lattice parameters measured for the crystals grown

All lattice dimensions are specified with respect to the pseudocubic subcell.

Crystal	Composition of the starting mixture (mole % K)	Composition obtained (mole % K)	Lattice parameters at room temperature			
			$a_p \sin \beta$ (Å)	$c_p \sin \beta$ (Å)	b_p (Å)	β
1	10	0.5-0.3	3.915	3.915	3.882	90° 40'
2	20	2-2.5	3.9251	?	3.8840	?
3	20	2-2.5	3.9249	3.9240	3.8835	?
4	90	25	3.9695	3.9630	3.9243	?
5	90	25	3.9747	3.9696	3.9391	90° 19'

2. Specimen preparation

Both single-crystal and powder specimens were used. The single crystals were grown in a Pt crucible by melting Na_2CO_3 , K_2CO_3 (Analar grade) and Nb_2O_5 (puriss, Fluka AG) together, with NaF as a flux. In this method, originally suggested by Wood (1951) for preparing pure sodium niobate, mixtures with varying Na/K ratio were heated at 1300°C for three hours and then slowly cooled to room temperature over a period of 24 hours. The crystals were extracted from excess NaF by boiling in water over several days. An analysis of the compositions of the crystals was made with an electron probe (by kind permission of the Department of Mineralogy and Petrology, Cambridge University). The results showed the compositions within a batch to vary over a range of 30 mole %. It also proved difficult to

find reasonably good and untwinned crystals suitable for structure determination, the difficulty becoming greater for higher K content. Table 1 gives the compositions of some of the single crystals examined with their lattice parameters.

The powder samples were prepared following closely the mixing and calcining procedure employed by Tenery & Hang (1968). The raw materials used were Na_2CO_3 , K_2CO_3 and Nb_2O_5 , and the mixtures were heat-treated at 1050°C for at least 24 hours.

3. Lattice-parameter determination

3.1. Lattice parameters at room temperature

X-ray diffraction powder patterns were measured on a Siemens diffractometer with $\text{Cu } K\alpha$ radiation from a graphite monochromator. The good resolution of the

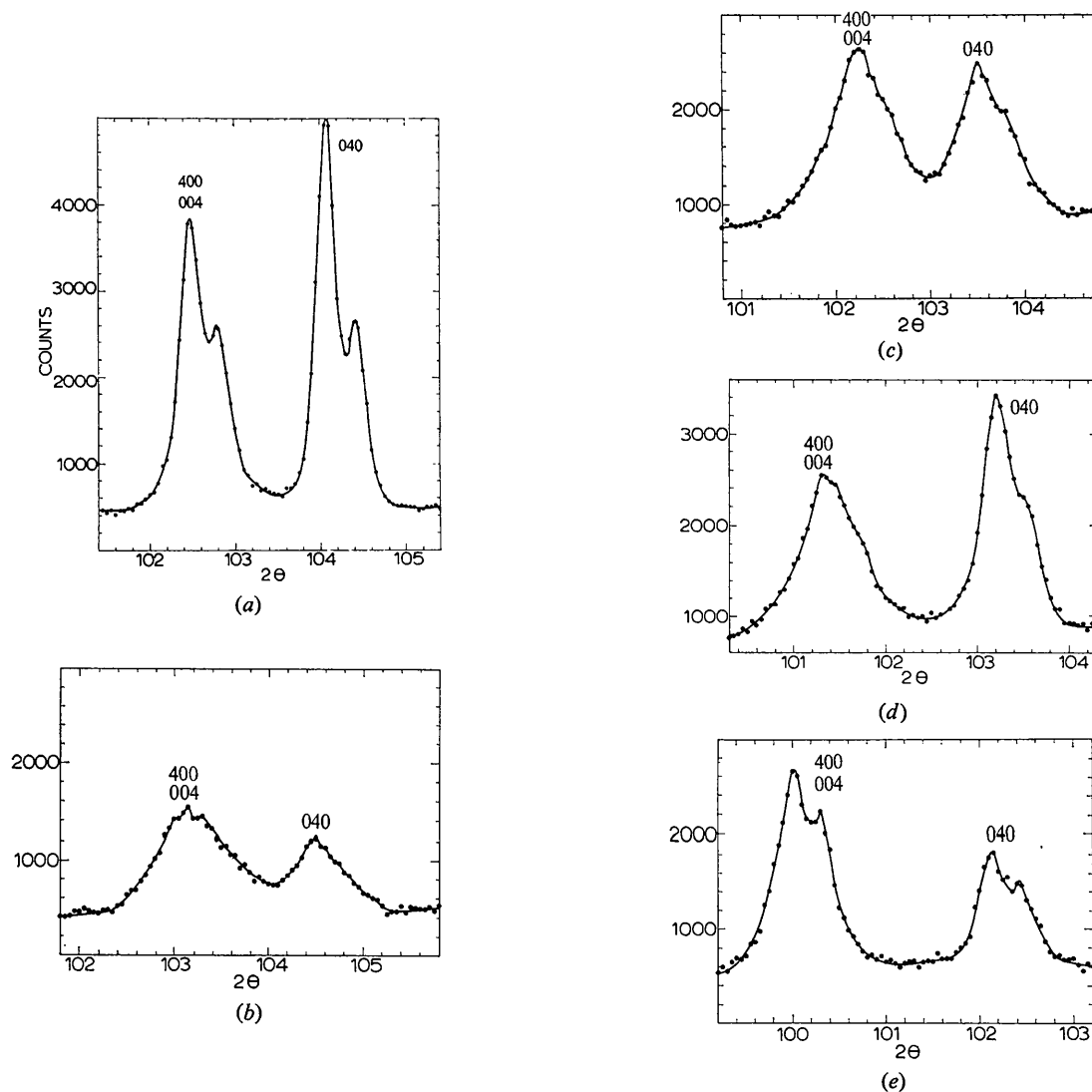


Fig. 2. Diffractometer traces of the $\{400\}$ complex from polycrystalline samples. (a) $x=0.02$. (b) $x=0.10$. (c) $x=0.20$. (d) $x=0.35$. (e) $x=0.80$.

diffraction lines into their components indicated that the specimens were of single phase. The values of the pseudocubic subcell axes a_p , $\sin \beta$ and b_p were obtained

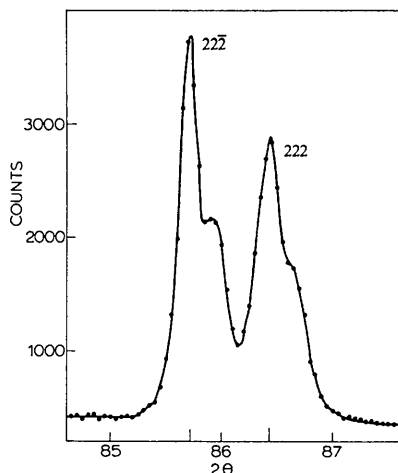


Fig. 3. Diffractometer trace of the 222 and $22\bar{2}$ reflexions for $x=0.02$.

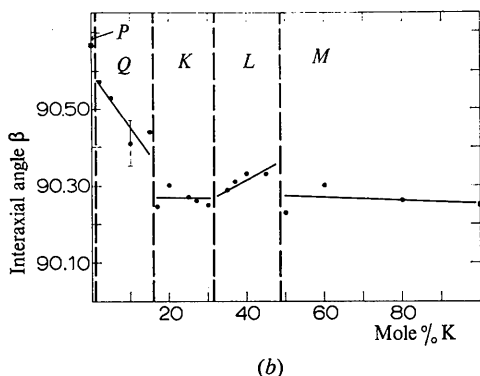
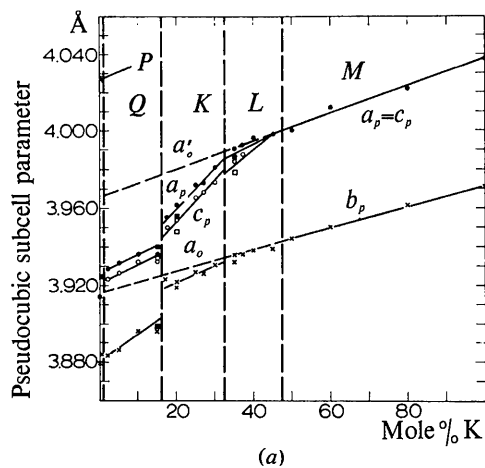


Fig. 4. (a) Pseudocubic subcell parameters at room temperature as a function of composition. The extrapolations a_o and a_o' are used in §4.1. (b) Interaxial angle β as a function of composition.

directly from the $N=16$ $\{400\}$ lines. β was calculated from the diffraction lines of the $N=12$ $\{222\}$ group according to

$$\cos \beta = -\frac{a_p c_p \sin^2 \beta}{16} \left[\frac{1}{d_{222}^2} - \frac{1}{d_{22\bar{2}}^2} \right]. \quad (3)$$

The unit-cell axes, a_p and c_p , can be obtained once β is calculated. The positions of the Bragg peaks were determined to $\pm 0.03^\circ$ in 2θ , corresponding to a precision of $\Delta a/a \approx 5 \times 10^{-4}$ and 0.06° in β . Fig. 2 shows some of the diffractometer traces of the $\{400\}$ reflexions. We have employed the so-called 'grid method' of Paatero (1969) to analyse the peak shapes. In this, a model curve is placed on different rows of a grid so that when rows are added together the experimental curve is obtained. A positive weight factor is used in the individual rows. The advantage of this technique is that there is no need to specify beforehand the number of components, since this is found automatically by the grid program.

Fig. 2(a) shows two groups of reflexions; the low-angle α_1, α_2 pair comes from 400 and 004 and it is not obvious to the eye that there are two separate spacings. The grid method immediately showed a small splitting in this low-angle pair when the α_1 and α_2 components of the 040 reflexion were used as the model curve. There is a difference in the peak half-widths which is consistent with this result. Thus we find that in phase Q the lattice parameters are such that $a_p \neq b_p \neq c_p$ in contrast to the results of earlier workers where it was found that $a_p = c_p$.^{*} Similar considerations apply for the curves at 10, 20 and 35 mole % K, where, again, we find three separate spacings [Figs. 2(b), (c) and (d)]. For 80 mole % K the difference in halfwidths is smaller than experimental error so that there is a strong probability of two lattice spacings being equal [Fig. 2(e)].

Fig. 3 shows the $\{222\}$ reflexion for 2 mole % K where it can be seen that there is quite a large splitting which leads to a very precise measure of β . From the equality of the half widths and sharpness of these reflexions it can be determined that the material is truly single phase. The lattice parameters calculated in this way are shown in Fig. 4(a) and 4(b). Two points are obvious from the figures. Firstly, with the exception of phase P, the pseudocubic subcell parameters a_p and c_p remain unequal across the solid-solution series, up to around 50 mole % K. This coupled with $\beta > 90^\circ$ means that the structures of phases Q, K and L are not orthorhombic. For phase M, however, $a_p = c_p$ with $\beta > 90^\circ$ and therefore it has an orthorhombic cell in

* This suggests that the true symmetry of phase Q is monoclinic rather than orthorhombic; moreover the tilt system of phase Q is not $a^-b^+a^-$ as given by the results of Wells & Megaw (1961), but rather $a^-b^+c^-$, i.e. three unequal tilts. The difference, however, is very small so that the original structure determination is probably sufficiently close to act as a working model. Recently this structure has been refined by neutron powder-profile analysis (Ahtee & Hewat, 1975) and agrees with our findings.

the rhombic orientation, *i.e.* with new axes according to the transformation:

$$\begin{matrix} a_o \\ b_o \\ c_o \end{matrix} \begin{pmatrix} a_p & b_p & c_p \\ 1 & 0 & 1 \\ 0 & 1 & 0 \\ 1 & 0 & 1 \end{pmatrix} \quad (4)$$

Secondly, there is a general increase in lattice parameters and an overall dropping and levelling-off in β with K content. From phase *K* to 100% potassium the increase in b_p is linear and almost equal to the increase in the $a_p=c_p$ axes in phase *M*. There is also a peculiar increase in β in phase *L*. Our results broadly agree with those of Tennery & Hang, but ours are somewhat more detailed.

3.2. Lattice parameters at higher temperatures

(a) $\text{Na}_{0.995}\text{K}_{0.005}\text{NbO}_3$ single crystal; phase *P* at room temperature: Fig. 5 shows the plot of lattice parameters of crystal 1 (see Table 1) as a function of temperature. These were measured by the continuous-recording procedure (Glazer, 1972*b*; Bett & Glazer, 1972). In this method several oscillation photographs are taken with a Weissenberg camera provided with a back-reflection film cassette of radius 57.3 mm. In our experiments the temperature was raised and lowered linearly at a rate of 0.30 to 0.50° min⁻¹. Simultaneously the

film cassette was displaced incrementally through $\frac{1}{2}$ mm with an exposure time of 10 min for each step. During each run the temperature stability was kept to within $\pm 0.25^\circ$. Cu $K\alpha$ radiation was used throughout and the crystal was oscillated around [001]. The reflexions used for the calculation of lattice parameters were of the {500} type.

The behaviour of the lattice parameters resembles that of pure NaNbO_3 (Glazer & Megaw, 1973) and confirms the electrical and optical observations made by Cross (1958). We also took a number of different Weissenberg photographs and compared them with those taken for pure NaNbO_3 . They confirmed the conclusion (Megaw & Wells, 1958) that at room temperature NaNbO_3 and $\text{Na}_{0.995}\text{K}_{0.005}\text{NbO}_3$ are of the same phase, with space group *Pnma* and tilt system $(a^-b^+a^-)_1^2 (a^-b^-a^-)_2^3 (a^-b^+a^-)_3^4$.

(b) $\text{Na}_{0.98}\text{K}_{0.02}\text{NbO}_3$ single crystal; phase *Q* at room temperature: Fig. 6 shows the continuous-recording photographs of crystal 2 (Table 1) taken with the method described above. The reflexions shown are the Cu $K\alpha_1$ - α_2 doublets of 500, 050 and 005 which occur within the same oscillation range because of twinning in the crystal. The most striking feature of this set of photographs is the occurrence of phase transitions at 300, 360, 460 and 610°C. Particularly noticeable is the large discontinuous increase in the lattice parameter,

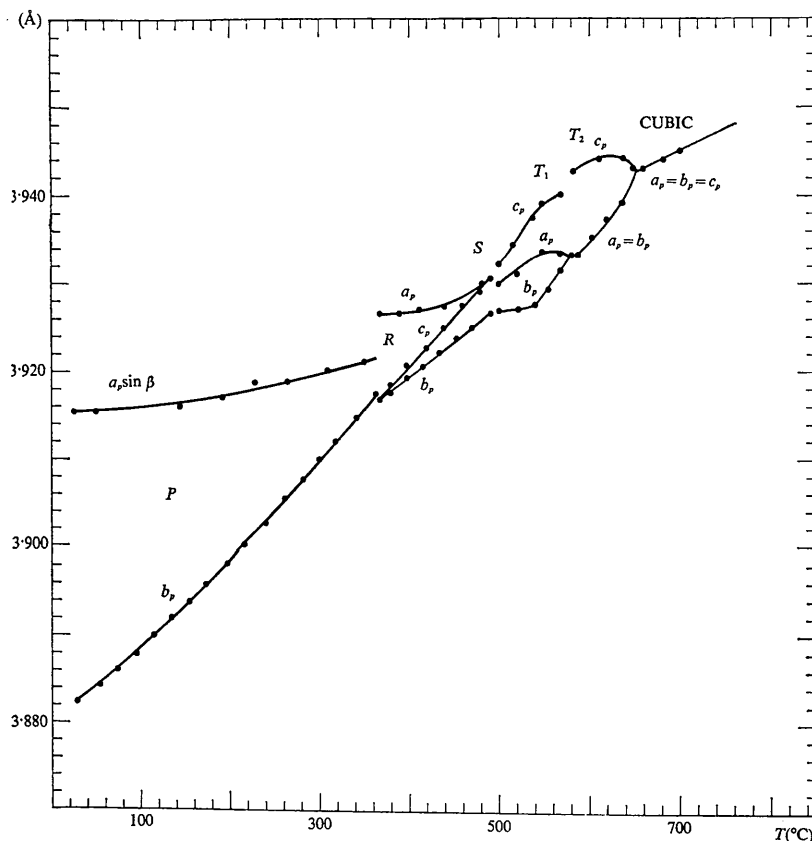


Fig. 5. Pseudocubic subcell parameters as a function of temperature for a crystal with $x=0.005$.

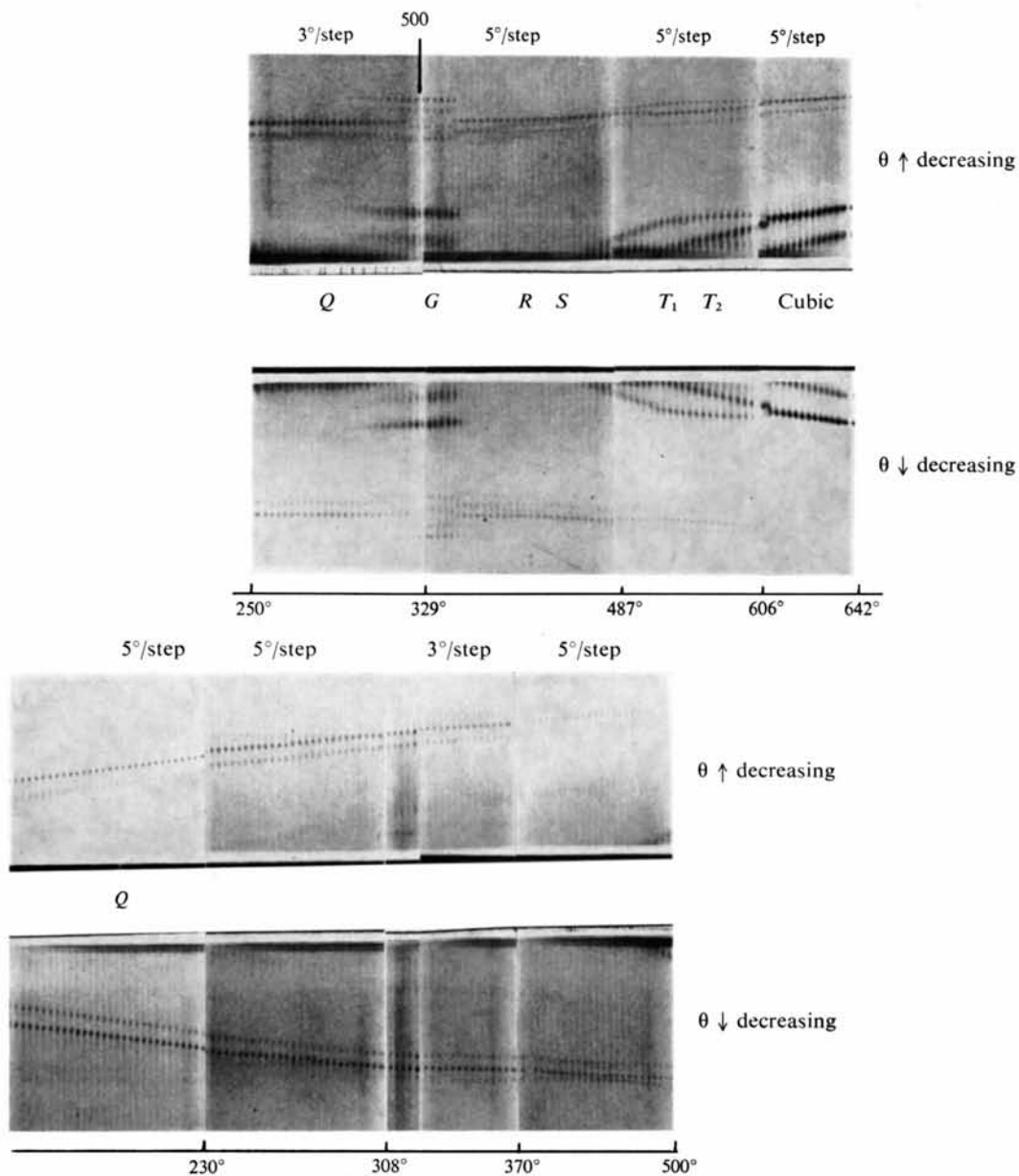


Fig. 6. X-ray continuous recording photographs for a single crystal with $x=0.02$. The upper set of photographs was taken for temperature increasing and the lower set for temperature decreasing. Notice the large change in the position of the 500 reflexion on going to phase *G*. Each reflexion is doubled due to the Cu $K\alpha_1$ - α_2 doublet.

a_p , at 300°C and corresponding drop at 360°C. This is a considerably larger effect than we are accustomed to seeing in this type of material, and it is remarkable that the crystal remains intact despite cycling through this temperature range! Reference to Fig. 1 shows that the crystal is in phase *G* at these temperatures. Co-existence of phases *Q* and *G* seems from these photographs to occur over the range 303 to 323°C.

Above the second transition at 360°C the familiar phases of NaNbO_3 re-establish themselves (compare with the phase diagram given by Glazer & Megaw, 1973). The structures of the upper phases were checked from zero- and half-layer Weissenberg photographs and compared with those of pure NaNbO_3 . This enabled us to identify them as *R*, *S*, T_1 , T_2 and cubic.

Because of twinning we can see both 500 and 005 reflexions above 300°C. A study of these twin-related reflexions shows the change-over in the lengths of the a_p and c_p axes in going to phase T_1 (where $c_p > a_p$) from phases *G*, *R* and *S* (where $c_p < a_p$). The same behaviour was reported by Glazer & Megaw (1973) for pure NaNbO_3 .

The complete lattice parameter plot is given in Fig. 7.* The similarity with the photographs is obvious.

* In this experiment the 005 reflexion in phase *Q* was not observed and hence c_p was not determined.

Large hysteresis is also shown for the b_p axis at the *Q*-to-*G* transition. By comparing Figs. 5 and 7 it can be seen that the ratio $a_p \approx c_p/b_p$ is much bigger in phase *Q* than in the antiferroelectric phase *P* which has anti-parallel displacements of Nb ions, roughly along [100] (two-corner displacements). This increase in both a_p and c_p is consistent with the fact that there are parallel cation displacements of the two-corner type in phase *Q*. The idea here is that the concerted action of parallel displacements gives rise to a net polarization, P_s , and since the lattice strain depends on P_s , this results in an increase in the appropriate unit-cell dimension, *i.e.* in this case, an increase in $a_p \approx c_p$. Similarly, in phase *G* we have a value of a_p which is much bigger than in phase *R*, and this may indicate that in phase *G* there are parallel cation displacements along [100]. Since here the displacements are *along* the axial direction the effect on the appropriate lattice spacing of making them parallel would be considerably larger. From the dielectric measurements of Cross (1958) and Shirane, Newnham & Pepinsky (1954) we know that phases *Q* and *G* show ferroelectric behaviour and this is consistent with our suggestion.

When the crystal is set about [010] we can see from zero-layer Weissenberg photographs that the unit cell changes from monoclinic in phase *Q* to orthorhombic in *G*. This is particularly clear from the 403 complex

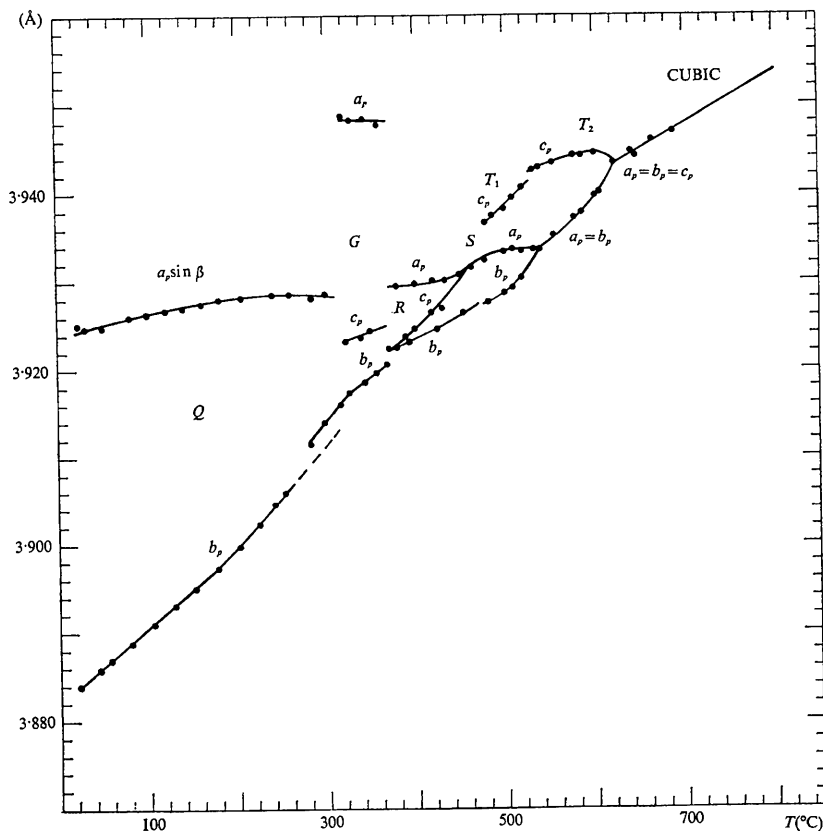


Fig. 7. Pseudocubic subcell parameter as a function of temperature for $x=0.02$ as measured from the continuous recording photographs in Fig. 6. Note the huge increase in a_p on going to phase *G*.

because β is related to these reflexions according to

$$\sin(\beta - 90^\circ) = \frac{\sin^2 \theta_{403} - \sin^2 \theta_{40\bar{3}}}{12\lambda^2 a^* c^*} \quad (5)$$

Thus when no difference in Bragg angle for 403 and $40\bar{3}$ is obtained, $\beta = 90^\circ$. This again supports our contention that phase *G* is the ferroelectric analogue of the antiferroelectric phase, *R*. Since in phase *R* the tilt system consists of pairs of $a^-b^+c^+$ layers alternating with single $a^-b^0c^+$ layers (Sakowski-Cowley, 1969; Glazer, 1972a) it is likely that the tilt system of phase *G* is either $a^-b^+c^+$ or $a^-b^0c^+$; the parallel nature of the cations suggests that the tilt system would be simple and not have the complex arrangement characteristic of phases *P* and *R* (this is further supported by the absence of any difference reflexions other than the half-integral type). Of the two possibilities, the most likely one is $a^-b^+c^+$ since the crystal eventually becomes $a^-b^+c^+$ but without Nb displacements (phase *S*) on heating above 460°C . It would be surprising if $a^-b^0c^+$ were to do this because it would mean addition of a tilt component with increasing temperature and this is not normally encountered in these types of material and, in any case, is thermodynamically unlikely. Assuming the $a^-b^+c^+$ structure and Nb displaced along [100] it is possible to suggest values for the Na/K displacements by considering the effects of the O configurations on them. However, until more definite evidence as to the tilt system becomes available we shall not attempt this here.

(c) $\text{Na}_{0.75}\text{K}_{0.25}\text{NbO}_3$ single crystal; phase *K* at room temperature: It proved difficult to find any reasonable crystals because of the coexistence of different compositions. Nevertheless with the continuous-recording procedure we could get some idea of the overall behaviour even in this phase. There are at least two phase transitions above room temperature at about 200 and 400°C . The lattice-parameter changes resemble that in pure KNbO_3 with the exception that in the room-temperature phase a_p and c_p are unequal.

(d) Powder samples of $\text{Na}_{1-x}\text{K}_x\text{NbO}_3$ with $0.02 < x < 0.60$: The lattice parameters of the powder samples were measured as a function of temperature with a Siemens X-ray diffractometer and an automatic, high-temperature furnace (Peljo, Vikberg & Paakkari, 1974). In this furnace the temperature was controlled to within $\pm 0.2^\circ\text{C}$ over the entire temperature range, 20 – 550°C . Monochromated Cu $K\alpha$ radiation was used and the line groups, $N = 12 \{222\}$ and $N = 16 \{400\}$ were slowly scanned at $0.05^\circ/10$ mins. The separation of the overlapping reflexions was more difficult at high temperatures than at room temperature because all three 400 reflexions tended to overlap. To overcome this difficulty we used the 400 reflexion of the highest-temperature phase, which is cubic, as the model reflexion for the 'grid' method whenever it was not possible to measure a discrete model reflexion at the particular temperature under study. When it was possible, it was always 040 that was used as the model reflexion. The

results obtained in this way are always less precise than those from single crystals; we found, for example, with $x = 0.02$, in which case single crystals were available as a check, that a typical precision of 1 part in 10^4 was obtained for single crystals whereas 1 part in 10^3 was obtained from overlapping reflexions from a powder sample. Since single crystals were not available at all compositions this was the only method that could be used. Nevertheless, the results do give a good indication of the behaviour of the lattice parameters with temperature.

Fig. 8 shows some typical lattice parameter plots obtained in this way. For $x = 0.10$ we see the *Q*-to-*G* transition, which is of first order. In phase *G* there is a fairly steep drop in c_p whereas a_p and b_p are linear with temperature. We have marked the region between 260 and 390°C as a new phase, *F*, for which we have some evidence based on difference reflexions

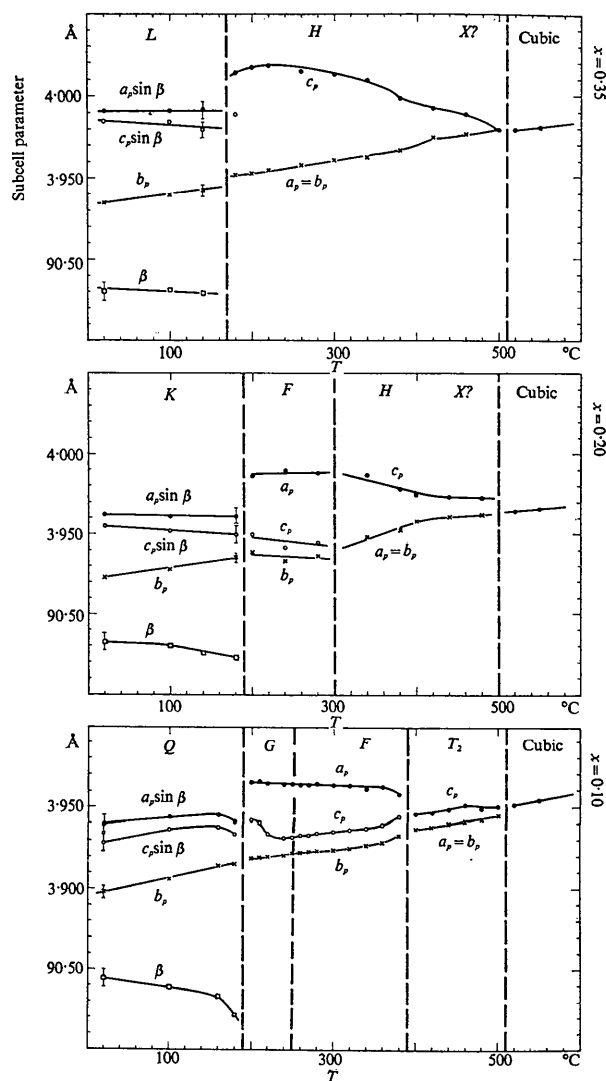


Fig. 8. Pseudocubic subcell parameters versus temperature for three compositions.

(see below). No obvious change at 260°C is found in the lattice parameters, however. For $x=0.20$ the room-temperature phase, K , becomes the new phase, F , at about 190°C (again the evidence in favour of phase F rather than G comes from the difference reflexions). At around 310°C phase F transforms to phase H . Because in this phase two axes appear to be equal we arbitrarily label them $a_p=b_p$ with the other axis as c_p . As we shall see, the probable tilt system indicates tetragonal symmetry. Our measurements seem to show that phase H extends to above 400°C. As we shall see later the difference reflexions disappear at 400°C and it is possible that this indicates a new, non-cubic phase. It may be that this is an extension of the T_2 phase across the phase diagram. However, this is unlikely as in T_2 the $a_p=b_p$ axes are smaller than in the cubic phase. This decrease results from the tilting of the octahedra in $a^0a^0c^+$ and can only give a larger value for a_p and b_p if large distortions are accepted. We shall denote this phase as $X?$.

For $x=0.35$ similar considerations apply. Here the room-temperature phase, L , becomes phase H on heating (as we shall see phase H is the same as the previously reported phase I). Again, phase H seems to extend to above 400°C (phase $X?$).

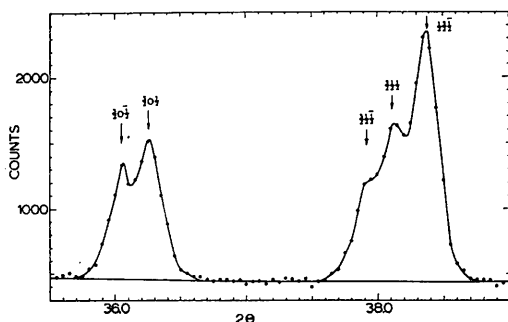


Fig. 9. Diffractometer trace of difference reflexions for $x=0.02$ (phase Q) at room temperature.

4. Tilting of octahedra

4.1. Observed difference reflexions at room temperature

As mentioned earlier the two types of octahedron tilt, in-phase and antiphase tilts, give rise to independent X-ray difference reflexions. These difference reflexions have half-integral indices when the lattice parameters are defined from the pseudocubic subcell and odd indices if they are defined from the true doubled unit cell. We consider two types of line groups namely $N=10/4$, $\{\frac{3}{2}0\frac{1}{2}\}$ and $N=11/4$, $\{\frac{3}{2}\frac{1}{2}\frac{1}{2}\}$, because we know that

a^+ tilts produce euu reflexions such as $0\frac{1}{2}\frac{3}{2}$,
 b^+ tilts produce ueu reflexions such as $\frac{1}{2}0\frac{3}{2}$,
 c^+ tilts produce uuu reflexions such as $\frac{1}{2}\frac{3}{2}0$,

and

a^- , b^- , c^- produce uuu reflexions such as $\frac{1}{2}\frac{1}{2}\frac{1}{2}$, $\frac{1}{2}\frac{1}{2}\frac{1}{2}$, $\frac{3}{2}\frac{1}{2}\frac{1}{2}$, etc.

In addition, the $\{\frac{3}{2}\frac{1}{2}\frac{1}{2}\}$, $N=14/4$, group was measured at room temperature. These reflexions also tell us about + tilts and act as an additional check. The elucidation of the tilt system relies, then, purely on the identification of any difference reflexions (Glazer, 1975). These extra reflexions are extremely weak, and it is not surprising, therefore, that past reports of them have been conflicting.

The relative intensities of the $\{\frac{3}{2}0\frac{1}{2}\}$ and $\{\frac{3}{2}\frac{1}{2}\frac{1}{2}\}$ reflexions were measured with respect to $\{110\}$ ($I=100$) with the Siemens diffractometer and monochromated Cu $K\alpha$ radiation. Fig. 9 shows a typical diffractometer trace of the appropriate difference reflexions for $x=0.02$ at room temperature (phase Q). The resolution is particularly high and the individual components of the difference reflexions can be seen. Table 2 summarizes the intensity measurements. With the aid of these reflexions we can identify the tilt systems in phases K and L , and these have been marked on the phase diagram in Fig. 1. The progressive simplification

Table 2. Intensities of difference reflexions at room temperature [measured on the scale $I(110)=100$], and tilt angles computed from them

Mole % K $h k l$	Q					K					L			
	2	5	10	15	17	20	25	27	30	35	37	40	45	
$\frac{3}{2} 0 \frac{1}{2}$	1.2	1.3	1.1	1.1	1.0	0.7	0.6	0.5	0.3	0.3	0.1	<0.1	—	
$\frac{3}{2} \frac{1}{2} \frac{1}{2}$	2.4	2.1	2.0	1.7	0.6	0.3	<0.1	—	—	—	—	—	—	
$\frac{3}{2} 1 \frac{1}{2}$	1.0	1.0	1.0	0.9	0.9	0.6	0.6	0.4	0.3	0.3	0.1	<0.1	—	
Tilt angles (°)														
α	7.5	7.0	6.5	6.4	6.0	4.2	<2.5	—	—	—	—	—	—	
β	9.5	10.0	9.8	9.0	9.0	7.4	7.2	5.5	5.0	5.0	3.0	<3	—	
γ	7.5	7.0	6.5	6.4	—	—	—	—	—	—	—	—	—	

Table 3. The progressive simplification of the tilt system with increasing K content

$Q(a^-b^+c^-)$	\rightarrow	$K(a^-b^+c^0)$	\rightarrow	$L(a^0b^+a^0)$	\rightarrow	$M(a^0a^0a^0)$	\rightarrow	$Na_{1-x}K_xNbO_3$
2 \rightarrow 15 mole % K		17 \rightarrow 30 mole % K		35 \rightarrow 45 mole % K		50 \rightarrow 100 mole % K		Composition
$S(a^-b^+c^+)$	\rightarrow	$T_1(a^-b^0c^+)$	\rightarrow	$T_2(a^0a^0c^+)$	\rightarrow	cubic ($a^0a^0a^0$)		$NaNbO_3$
480° \rightarrow 520°C		520° \rightarrow 575°C		575° \rightarrow 640°C		640°C \rightarrow		Temperature

of the tilt system as the K content is increased resembles to some extent that found in pure NaNbO_3 with increasing temperature (Table 3). The location of the phase boundaries with composition is only known to about 5 mole % because it is difficult to decide whether a particular sample is in one phase or another. If a difference reflexion is not observed one cannot say for certain that it is absent.

Values of the tilt angles, α , β and γ , were obtained by fitting the calculated intensities of Table 2 to the observed ones with trial models having varying tilt angles (we assumed that tilt angle α = tilt angle γ in phase Q). The final results are compiled in Table 2 and drawn against composition in Fig. 10. Preferred orientation has a large effect on the intensities when pressed powder samples are used. By harmonic analysis (Järvinen, Merisalo, Pesonen & Inkinen, 1970) it was found that the [100] direction was the most strongly preferred and this meant that the ratio of $(I_{\text{corr}} - I_{\text{meas}})/I_{\text{meas}}$ was -0.28 for the $\{100\}$ reflexions. For the 110 reflexions which we used as a reference in the tilt-angle calculations the corresponding ratio was -0.04 and for the $\{\frac{3}{2}0\frac{1}{2}\}$ and $\{\frac{3}{2}\frac{1}{2}\frac{1}{2}\}$ reflexions -0.05 and -0.02 respectively. The intensity measurements were not made carefully enough to allow any corrections to be made but it can be concluded that our estimates of tilt angles are probably slightly on the high side.

Provided the octahedra are undistorted, the tilt angles can also be related to the lattice parameters by

$$\begin{aligned} a_p &= a_o \cos \beta \cos \gamma \\ b_p &= a_o \cos \alpha \cos \gamma \\ c_p &= a_o \cos \alpha \cos \beta \end{aligned} \quad (6)$$

where a_o is the distance between Nb atoms (around 4\AA). Now, by comparing our measured tilt angles with the lattice parameters it is possible to say something about the distortions of the octahedra:

(a) Across phase Q all the tilt angles decrease; this means according to (6) that all the lattice parameters should increase. As seen in Fig. 4(a) this appears to be true.

(b) At the boundary between the phases Q and K the γ tilt angle vanishes abruptly. This is associated with the abrupt increase in both a_p and b_p . At the same time, the loss of one tilt to give a two-tilt system, with one + tilt and one - tilt, would tend to lead to orthogonal axes [see the discussion by Glazer (1972a) on the relationship between the signs of tilts and interaxial

angle]. This agrees well with the drop in β towards 90° shown in Fig. 4(b). According to (6), the loss of γ tilt should not effect c_p ; that c_p is seen to increase with a_p means that there is some considerable elongation of the octahedra along [001].

(c) Across phases K and L , the β tilt decreases more-or-less linearly with composition. This corresponds to the steeper but generally continuous increase in a_p and c_p . In phase L the non-equivalence of a_p and c_p , despite the equivalence of α and γ tilts (identically zero), means that there is still some residual distortion of the octahedra in the (010) plane, but considerably less than in phase K . Finally, when the β tilt is lost, $a_p = c_p$ in phase M , the difference between $b_p = c_p$ being due to a flattening of the octahedra along [010]. This latter distortion is present across the entire series. In order to explain this we must assume that, since phases M , Q and P are known to possess two-corner Nb displacements, then so do phases K and L , and as a consequence of this dipole being confined to (010) planes, the octahedra generally tend to be larger in the [100] and [001] directions than in the [010] direction.

By extrapolating b_p from phase M we have the change of a_o with K content. The a_p and c_p axes are affected in a different manner by Nb displacements lying in the (010) plane and we can take this into account by extrapolating a_p and c_p from phase M . The tilt angles calculated from (6) using these a_o values are given in Table 4. It can be seen that this rough approximation gives the general behaviour of the tilts although they all tend to be underestimated by about 40%.

Finally, we have observed a few very weak lines of the *eue* type. This is not consistent with tilting but can arise either through antiparallel cation displacements

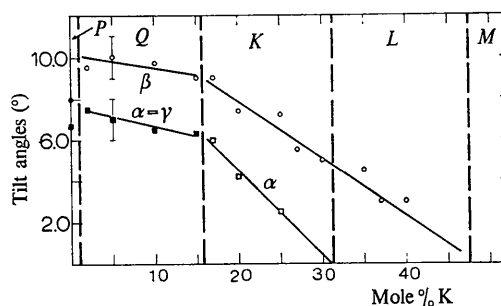


Fig. 10. Tilt angles as a function of composition computed from the intensities of the difference reflexions.

Table 4. Values of tilt angles at room temperature estimated from the lattice parameters

Mole % K	Q					K					L		
	2	5	10	15	17	20	25	27	30	35	37	40	45
a_o (\AA)*	3.917	3.919	3.922	3.925	3.926	3.927	3.930	3.931	3.933	—	—	—	—
a'_o (\AA)*	3.967	3.969	3.973	3.977	3.978	3.980	3.984	3.984	3.987	3.991	3.993	—	—
α ($^\circ$)	5.3	5.3	4.9	4.4	3.7	3.2	2.6	1.6	2.2	—	—	—	—
β ($^\circ$)	6.3	6.2	6.5	6.7	6.2	5.7	4.8	4.3	3.1	3.4	2.2	—	—
γ ($^\circ$)	5.3	5.3	4.9	4.4	—	—	—	—	—	—	—	—	—

* a_o extrapolated from b_p , a'_o extrapolated from $a_p = c_p$; in the calculations $\langle a_p \rangle = (a_p + c_p)/2$.

or through ordering of the Na and K atoms in an alternating sequence. We find reflexions $\{1\frac{3}{2}0\}$, $\{1\frac{3}{2}1\}$, $\{2\frac{1}{2}1\}$ and $\{2\frac{3}{2}0\}$ for $x=0.02$, $\{1\frac{3}{2}1\}$, $\{2\frac{1}{2}1\}$, and $\{2\frac{3}{2}0\}$ for $x=0.10$, $\{1\frac{3}{2}1\}$ and $\{2\frac{1}{2}1\}$ for $x=0.20$, and $\{1\frac{3}{2}1\}$ for $x=0.35$. The intensities of these reflexions are normally less than 1/20th of the difference reflexions due to tilting and thus are very weak indeed. Since at these compositions ferroelectricity has been reported it is unlikely that these reflexions arise from antiparallel cation displacements. This is supported by recent neutron profile analysis of phase *Q* (Ahtee & Hewat, 1975). The most likely explanation therefore is ordering of the Na and K ions along an axial direction. The loss of intensity with increasing x means that this ordering also decreases with increasing x .

4.2. Observed difference reflexions at higher temperatures

In Fig. 11 we show the relative intensities of the $\{\frac{3}{2}0\frac{1}{2}\}$ -type and $\{\frac{3}{2}\frac{1}{2}\frac{1}{2}\}$ -type difference reflexions as a function of temperature for samples with $x=0.02$, 0.10, 0.20 and 0.35. These two types of reflexion tell us about + and - tilts respectively. For $x=0.02$ we see that in phase *Q* there is a steady decrease in intensity of the $\{\frac{3}{2}\frac{1}{2}\frac{1}{2}\}$ line with temperature whereas the $\{\frac{3}{2}0\frac{1}{2}\}$ line is more-or-less constant with a slight rise just below the 270°C transition. Assuming that in phase *Q* we can write tilt angle $\alpha \approx$ tilt angle γ the decrease in intensity

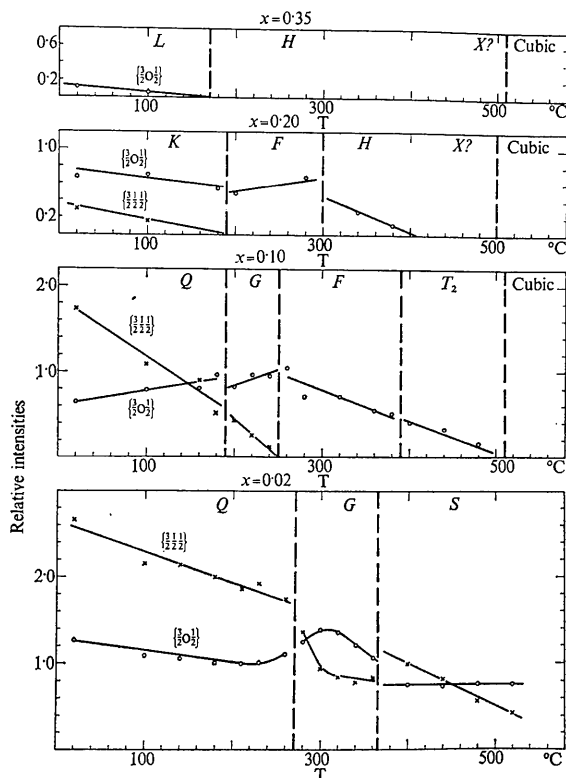


Fig. 11. Relative intensities of difference reflexions as a function of temperature for four compositions.

of $\{\frac{3}{2}\frac{1}{2}\frac{1}{2}\}$ means a decrease in both tilt angles. At the transition to phase *G* the $\{\frac{3}{2}\frac{1}{2}\frac{1}{2}\}$ intensity drops steeply whereas the $\{\frac{3}{2}0\frac{1}{2}\}$ intensity rises correspondingly. This is consistent with our earlier suggestion (Ahtee & Glazer, 1974) that the tilt system of phase *G* is $a^-b^+c^+$ since this results from $a^-b^+c^-$ (phase *Q*) by the loss of the c^- tilt and subsequent replacement by c^+ . Further evidence for tilt system $a^-b^+c^+$ comes from Fig. 7 where we see the large a_p axis indicating probably parallel cation displacements along [100]. Such displacements are more likely in a structure with tilt system $a^-b^+c^+$ than in one with two - tilts as is apparent from a study of the environment of the Na/K atoms under these tilt systems. A rough rule is that when there are displacements their components are parallel to the - tilt axes.

For $x=0.10$ we again see the decrease in α and γ tilts in phase *Q*, and the change to phase *G*. Notice that in phase *G* the $\{\frac{3}{2}\frac{1}{2}\frac{1}{2}\}$ intensity becomes zero, or at least below the level of measurement. The next-highest phase above 250°C, therefore, probably does not possess a - tilt and we suggest the tilt system $a^0b^+c^+$. Although the lattice parameter plot (Fig. 8) showed no obvious discontinuity at this temperature the apparent loss of $\{\frac{3}{2}\frac{1}{2}\frac{1}{2}\}$ intensity does suggest that there is a transition at 250°C. The resulting phase therefore is a new one and we have labelled it *F*. From Fig. 8 there is an obvious change in lattice parameters at around 390°C indicating another transition. This is probably accompanied by a loss of a + tilt to give $a^0a^0c^+$ (the T_2 phase) in agreement with the result of Cross (1958). We see in Fig. 11 a correspondingly low intensity for the $\{\frac{3}{2}0\frac{1}{2}\}$ -type line.

For $x=0.20$ the room-temperature phase is *K*. Here we find a loss of the - tilt at 190°C to give a phase with a tilt system the same as in phase *F*. At 300°C a possibly discontinuous drop of intensity of the $\{\frac{3}{2}0\frac{1}{2}\}$ line indicates a loss of a + tilt to give $a^0a^0c^+$. However this may not be the same phase as T_2 if we are to accept the presence of ferroelectricity in this phase as measured by Shirane, Newnham & Pepinsky (1954). Moreover, the large difference between c_p and $a_p=b_p$ in this phase (Fig. 8) is also consistent with parallel cation displacement along [001]. Therefore we shall tentatively call it phase *H*.

Finally for $x=0.35$ we see that the room-temperature structure, phase *L*, seems to lose continuously intensity of the $\{\frac{3}{2}0\frac{1}{2}\}$ -type reflexion. The jump in lattice parameter c_p (Fig. 8) suggests parallel cation displacements along [001] and so the phase above 170°C, therefore, is probably the same as phase *H*.

5. Summary

In this section we shall summarize the results of all these experiments dealing with each phase in turn. We shall not discuss the phases of pure NaNbO_3 (*P*, *R*, *S*, T_1 and T_2) or of pure KNbO_3 (which we have labelled *M*, *J*) since they have been dealt with fully elsewhere.

In each case, we shall give some suggestion as to likely space groups. All the phases discussed here have been reported as ferroelectric and so we can assume that there are displaced cations in the structure and that the space groups are non-centrosymmetric.

Phase Q

As this is a ferroelectric phase we expect parallel cation displacements. The lattice parameters are given by

$$a_p \neq b_p \neq c_p, \quad \alpha = \gamma = 90^\circ, \quad \beta > 90^\circ.$$

This together with the presence of difference reflexions of the type $\{\frac{3}{2}0\frac{1}{2}\}$ and $\{\frac{3}{2}\frac{1}{2}\frac{1}{2}\}$ indicates tilt system $a^-b^+c^-$ (Glazer, 1972a, 1975). The space group of $a^-b^+c^-$ is (No. 11) $B12_1/m1$ on pseudocubic axes. If we now take axes defined by $\frac{1}{2}\mathbf{a}_p + \frac{1}{2}\mathbf{c}_p, \mathbf{b}_p, -\frac{1}{2}\mathbf{a}_p + \frac{1}{2}\mathbf{c}_p$ the space-group symbol is $P2_1/m$ (2nd setting) with the positions of the cations on centres of inversion. However, the presence of ferroelectricity means that this centre is absent and that the cations are displaced so that the true space group is either (No. 6) Pm or (No. 4) $P2_1$. We dispense with $P2_1$ since this would automatically produce antiparallel cation displacements on successive layers perpendicular to b_p . The most probable space group is therefore (No. 6) Pm . The mirror planes are between (010) planes of octahedra and the Na/K ions lie on them. The Nb ions on the other hand are at general positions. Because of the near equality of a_p and c_p the displacements will be approximately two-corner displacements.

Phase K

As this is reported to be ferroelectric we again assume parallel cation displacements. The lattice parameters are

$$a_p \neq b_p \neq c_p, \quad \alpha = \gamma = 90^\circ, \quad \beta > 90^\circ.$$

The difference reflexions observed were of the type $\{\frac{3}{2}0\frac{1}{2}\}$ and $\{\frac{3}{2}\frac{1}{2}\frac{1}{2}\}$. We have assumed that this phase is obtained from phase Q by loss of a tilt (Ahtee & Glazer, 1974) to give $a^-b^+c^0$. The space group for this tilt system is (No. 63) $Bbmm$. For this space group the Nb ions would lie on centres of inversion given by the 4(a) and 4(b) sites and the Na/K ions would be on 8(d) sites which are also centres of inversion. The occurrence of ferroelectricity suggests a non-centrosymmetric structure and this together with the lattice parameters gives space group (No. 4) $B2_1$ or (No. 6) Bm . If the displacements are approximately along b_p the latter applies. We expect that since the room-temperature structures of the other phases have two-corner displacements then the same possibly applies here. The most likely space group on this basis is therefore (No. 6) $Bm \equiv Pm$.

Phase L

Here again ferroelectric behaviour has been observed. The lattice parameters are

$$a_p \neq b_p \neq c_p, \quad \alpha = \gamma = 90^\circ, \quad \beta > 90^\circ.$$

This time the only difference reflexions observed are the $\{\frac{3}{2}0\frac{1}{2}\}$ type and assuming that this phase is formed from phase K by progressive loss of tilt it belongs to tilt system $a^0b^+a^0$. This tilt system belongs to (No. 127) $C4/mmb$ with axes chosen so that b_p becomes the tetragonal c axis, *i.e.* tilt system is $a^0a^0c^+$. Again the obvious lack of a centre of inversion together with the lattice parameters suggests a monoclinic space group such as (No. 4) $B2_1$ or (No. 6) Bm . These correspond to space groups $P2_1$ and Pm when new axes, $\mathbf{a}_p + \mathbf{c}_p, \mathbf{b}_p, -\mathbf{a}_p + \mathbf{c}_p$, are taken. The a_p and c_p axes are approximately equal and much larger than b_p (Fig. 8). This suggests that the displacements of the cations will be more or less perpendicular to b_p . In this case we cannot have space group $P2_1$ as this would result in roughly antiparallel sheets of dipoles perpendicular to b_p . If we assume Pm the Na/K atoms lie on the mirror planes and therefore are displaced in directions exactly perpendicular to b_p . The fact that $\beta > 90^\circ$ suggests two-corner displacements approximately along $[10\bar{1}]$.

Phase G

The lattice parameters are

$$a_p \gg b_p \neq c_p, \quad \alpha = \beta = \gamma = 90^\circ.$$

As we have discussed earlier, the large value of a_p suggests parallel cation displacements along $[100]$. The difference reflexions observed are of the $\{\frac{3}{2}0\frac{1}{2}\}$ and $\{\frac{3}{2}\frac{1}{2}\frac{1}{2}\}$ type and as discussed earlier we propose the tilt system $a^-b^+c^+$. This belongs to space group (No. 59) $Pnmm$. If the centre of inversion is removed with displacements allowed along $[100]$ we have (No. 25) $P2mm$. The two perpendicular mirror planes bisect the (010) and (001) planes of octahedra. This puts the Na/K atoms on twofold axes, *i.e.* they are on 1(a), 1(b), 1(c) and 1(d) sites. As there are eight Na/K atoms per unit cell, there are therefore eight possible values for the x coordinate. The Nb atoms lie at general positions so that they can be displaced in any direction. With this structure for phase G the transition from Q to G involves the reversal of sign of the c^- tilt. This is energetically difficult because it involves the squeezing of O atoms between the Nb atoms as the sense of tilt is reversed. This fits in well with the observation of large discontinuities in the lattice parameters at this transition.

Phase F

The lattice parameters are

$$a_p \gg b_p \neq c_p, \quad \alpha = \beta = \gamma = 90^\circ$$

and the occurrence of difference reflexions of the type $\{\frac{3}{2}0\frac{1}{2}\}$ suggests the loss of the a^- tilt in phase G. The tilt system then becomes $a^0b^+c^+$ which has space group (No. 71) $Immm$. Again if we assume the loss of centre of inversion with displacements along $[100]$ (this is because $a_p \gg b_p$ and c_p and (6) would otherwise lead to a smaller a_p when there is no α tilt) (No. 44) $I2mm$ is obtained. As in phase F the Na/K atoms lie on two-

fold axes, which in this case are $2(a)$ and $2(b)$ sites. The centring however ensures that the displacements of the Na/K atoms are more restricted, *i.e.* there are only four possible values for the x coordinate. The Nb atoms are distributed along the 2_1 axis parallel to $[100]$ so that unless antiparallel displacements are allowed they must be displaced in directions close to this 2_1 axis.

Phase H

The lattice parameters are

$$a_p = b_p < c_p, \quad \alpha = \beta = \gamma = 90^\circ$$

and only difference reflexions of the type $\{\frac{3}{2}0\frac{1}{2}\}$ are found. We assume that phase *H* develops from phase *F* by loss of a tilt to the $a^0a^0c^+$ tilt system. Equations (6) show that the tilt is probably about $[001]$ because c_p is so much larger than $a_p = b_p$. Moreover, the shape of the difference reflexion showed that it consisted of only one reflexion which with the axes chosen here would index as $\frac{3}{2}\frac{1}{2}0$. The tilt-system space group is (No.

127) $C4/mmb$. If we assume displacements along $[001]$ the tetragonal symmetry is retained in agreement with the lattice parameters. The space group then becomes (No. 100) $C4mb$. In this case, Nb atoms are on the fourfold axis, *i.e.* at $2(a)$ sites and the Na/K atoms lie on twofold axes, *i.e.* $2(b)$ sites. Thus all displacements must be exactly along $[001]$.

Phase X?

As we have seen earlier, there is evidence of two lattice spacings in this region of the phase diagram which had previously been considered as cubic. Our observations therefore suggest that there may be a tetragonal distortion. If we now accept that there is no observation of ferroelectric behaviour here the most likely structure is that of T_2 , *i.e.* it has tilt system $a^0a^0c^+$ with space group (No. 127) $C4/mmb$. We have not observed any difference reflexions such as $\frac{3}{2}\frac{1}{2}0$ which would be expected as a result of the c^+ tilt but this may be simply that the intensity is below the level of sensitivity of our measurements (*i.e.* the γ tilt angle is very small). It

Table 5. Summary of sequence of phase transitions in $\text{Na}_{1-x}\text{K}_x\text{NbO}_3$

Composition x	Phase	Transition temperature (°C)	Tilt system	Approximate displacement direction	Space group	
0.02	<i>Q</i>	↓ 270	$a^-b^+c^-$	Two-corner $[10\bar{1}]$	<i>Pm</i>	
	<i>G</i>	↓ 360-380	$a^-b^+c^+$	One-corner $[100]$	<i>P2mm</i>	
	<i>R</i>	↓ 400	$a^-b^+c^+$; $a^-b^0c^+$	One-corner, antiparallel $[100]$	<i>Pnmm</i>	
	<i>S</i>	↓ 470	$a^-b^+c^+$	—	<i>Pnmm</i>	
	<i>T</i> ₁	↓ 530	$a^-b^0c^+$	—	<i>Ccmm</i>	
	<i>T</i> ₂	↓ 620	$a^0a^0c^+$	—	<i>C4/mmb</i>	
	Cubic	↓	$a^0a^0a^0$	—	<i>Pm3m</i>	
	0.10	<i>Q</i>	↓ 190	$a^-b^+c^-$	Two-corner $[10\bar{1}]$	<i>Pm</i>
		<i>G</i>	↓ 250	$a^-b^+c^+$	One-corner $[100]$	<i>P2mm</i>
<i>F</i>		↓ 390	$a^0b^+c^+$	One-corner $[100]$	<i>I2mm</i>	
<i>T</i> ₂		↓ 510	$a^0a^0c^+$	—	<i>C4/mmb</i>	
Cubic		↓	$a^0a^0a^0$	—	<i>Pm3m</i>	
0.20		<i>K</i>	↓ 190	$a^-b^+c^0$	Two-corner $[10\bar{1}]$	<i>Pm</i>
	<i>F</i>	↓ 300	$a^0b^+c^+$	One-corner $[100]$	<i>I2mm</i>	
	<i>H</i>	↓ 410	$a^0a^0c^+$	One-corner $[001]$	<i>C4mb</i>	
	<i>X?</i>	↓ 500	$a^0a^0c^+?$?	<i>C4/mmb?</i>	
	Cubic	↓	$a^0a^0a^0$	—	<i>Pm3m</i>	
	0.35	<i>L</i>	↓ 170	$a^0b^+a^0$	Two-corner $[10\bar{1}]$	<i>Pm</i>
<i>H</i>		↓ 400	$a^0a^0c^+$	One-corner $[001]$	<i>C4mb</i>	
<i>X?</i>		↓ 510	$a^0a^0c^+?$?	<i>C4/mmb?</i>	
Cubic		↓	$a^0a^0a^0$	—	<i>Pm3m</i>	

is tempting to suggest that this is an extension of phase T_2 across the phase diagram. This has the advantage of fitting in well with the phases below it such as F , H and possibly J since the transitions between it and these phases can be accomplished by simple loss of displacements or tilt. However, as explained earlier, the lattice parameters indicate that if the tilt system is $a^0a^0c^+$ then the octahedra must be fairly distorted.

In Table 5 we show the complete sequence of transitions with our suggested space groups. It would be intriguing to see how much of what we have derived from indirect evidence holds true. Probably the most fruitful way of doing this is to use the Rietveld (1969) neutron profile analysis method and a programme of research is in progress to elucidate this problem.

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