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AN X-RAY STUDY OF PHASE TRANSITIONS IN $NaNbO_3$

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A detailed study has been made of polycrystalline $NaNbO_3$ in the range from room temperature to 700°C. A new second-order phase transition is detected at 430°C; the subcell of $NaNbO_3$ is monoclinic in the range 360-430°C ($NaNbO_3$ is actually orthorhombic), the parameters being $a = c \cong b$, $\beta > 90°$; this result agrees with optical evidence. Proof is obtained of a transition at 470°C, which previously had been detected only optically. The symmetry of $NaNbO_3$ at -196°C is the same as that at room temperature. The relation of the dielectric parameters to the types of phase transitions is discussed.

Introduction

Sodium niobate, $NaNbO_3$, is a compound of ABO_3 type that is of special interest; it has several phase transitions within a fairly narrow temperature range, and it resembles $PbZrO_3$ and $PbHfO_3$ in being an antiferroelectric. Some of the transitions are accompanied by anomalous changes in the dielectric parameters; some are not. It is important to establish the nature of these transitions in $NaNbO_3$ in order to elucidate the behavior of this type of compound.

There are many papers on the dielectric, optical, and x-ray features of $NaNbO_3$ [1, 11], but the various methods have not given consistent results on the phase transitions. Dielectric and optical measurements on monocrystals [10] at elevated temperatures have shown that transitions occur at about 360, 470, 520, and 640°C. The x-ray results for temperatures above 300°C [4, 9, 11] are in conflict as to the symmetry and transitions (the unit cell is slightly distorted). Optical studies [4] indicate that $NaNbO_3$ is orthorhombic at 300°C, whereas the x-ray results from the same work indicate that is tetragonal. The birefringence varies with temperature in a manner such as to indicate that $NaNbO_3$ is still orthorhombic above the transition temperature of 360°C [9, 10], whereas the x-ray results [9, 11] indicate that it is tetragonal.

Wood [4] explains these discrepancies by saying that the optical methods are most sensitive to any displacement of the Na and that the x-rays ones are most sensitive for Nb. Shirane et al.[9] suppose that x-ray methods are generally less sensitive to small degrees of distortion in the structure.

Only Cu radiation has so far been used in the x-ray studies on $NaNbO_3$. Our experience has shown that the proper choice of wavelength is decisive in determining the symmetry and small distortions of the unit cell [12, 13].

Methods

Choice of Radiation. The lines most sensitive to small distortions in the structure are the ones to be used in order to detect symmetry changes. The splitting must be such as to allow of only one interpretation, and the lines should lie at large angles of scattering.

We used Cu radiation to examine $NaNbO_3$ at liquid-nitrogen temperature. Some of the patterns recorded at higher temperatures were produced with Cu and Cr radiations. We found that the splitting of the 422 line ($\theta \sim 75°$) could not be established unambigously at and above 300°C if Cu radiation was used.

The best is Fe radiation if the range is from room temperature to 700°C; here the splittings in the 222 ($\theta \sim 60°$) and 400 ($\theta > 80°$) lines allow of only one interpretation. In particular, orthorhombic $NaNbO_3$, which has a pseudomonoclinic unit cell with $a = c$, gives a 222 line split into two components 222 and $22\bar{2}$ of equal intensity (this is the result of β alone), while the splitting of the 400 line into 400 and 040 lines is the result of the difference between a and b only. A rhomobohedral distortion also causes the 222 line to split, but here the 222 line is three times as intense as the $22\bar{2}$ line; further, the 400 line does not split at all. Tetragonal distortions do not split 222, while the intensity ratio of the 400 and 004 lines resulting from 400 is not that found for monoclinic distortion.

Thus, the three types of distortion in $NaNbO_3$ are readily differentiated by means of Fe radiation, as Fig. 1 shows for several different temperatures.

Apparatus and Conditions. The film was set asymmetrically in the URS-55 equipment, which was fitted with a PVRK-114 precision high-temperature camera (diameter about 114 mm) for the work with $NaNbO_3$. A similar camera also 114 mm in diameter was used for the low-temperature work. (The two cameras were designed and made at the Karpov Institute of Physical Chemistry.) The specimens were cylinders not more than 0.4 mm in diameter and about 5 mm long. The Agfa x-ray film required an exposure of 25-30 hr on unfiltered Fe radiation. An ÉPV-01 potentiometer kept the temperature variation less than 1%.

Subcell of $NaNbO_3$. Megaw's method [14], which we have used before [12, 13], was applied to find the parameters of the pseudomonoclinic cell. If a = c but b differs slightly from these, and if β differs only slightly from 90° ($|\cos\beta| \ll 1$), we have $b = a(1 + y)\sin\beta$, in which $y \ll 1$. Then, apart from second-order and higher terms, we have

$$d_{hkl} = \frac{a\sin\beta}{\sqrt{N}}\left(1 + \frac{k^2 y}{N} + \frac{hl\cos\beta}{N}\right),$$

in which $N = \Sigma h_i^2$.

We can find β from

$$\cos\beta = \frac{(\sin\Theta_{hk\bar{l}} - \sin\Theta_{hkl})\,N}{(\sin\Theta_{hk\bar{l}} + \sin\Theta_{hkl})\,hl}. \qquad (2)$$

This β was found to ±2.5' from the 422 lines ($\theta \sim 75°$) by means of Cu radiation at temperatures up to 300°C, and also from the 222 lines ($\theta \sim 60°$) to ±4' by means of Fe radiation. Only Fe radiation was used at temperatures above 300°C.

The other cell constants were determined only from the 400 lines, which split into 400 and 040. Then (1) gives us for these components that

$$d_{400} = \frac{a\sin\beta}{4}; \quad d_{040} = \frac{a\sin\beta}{4}(1 + y),$$

so $y = \frac{\sin\theta_{400}}{\sin\theta_{040}} - 1$ with an error of ±0.0003. From β and y we find a, b, and the volume v of the cell; here $\Delta a = \pm 0.0006$, $\Delta b = \pm 0.0015$A, $\Delta v = \pm 0.04_5 A^3$. This same

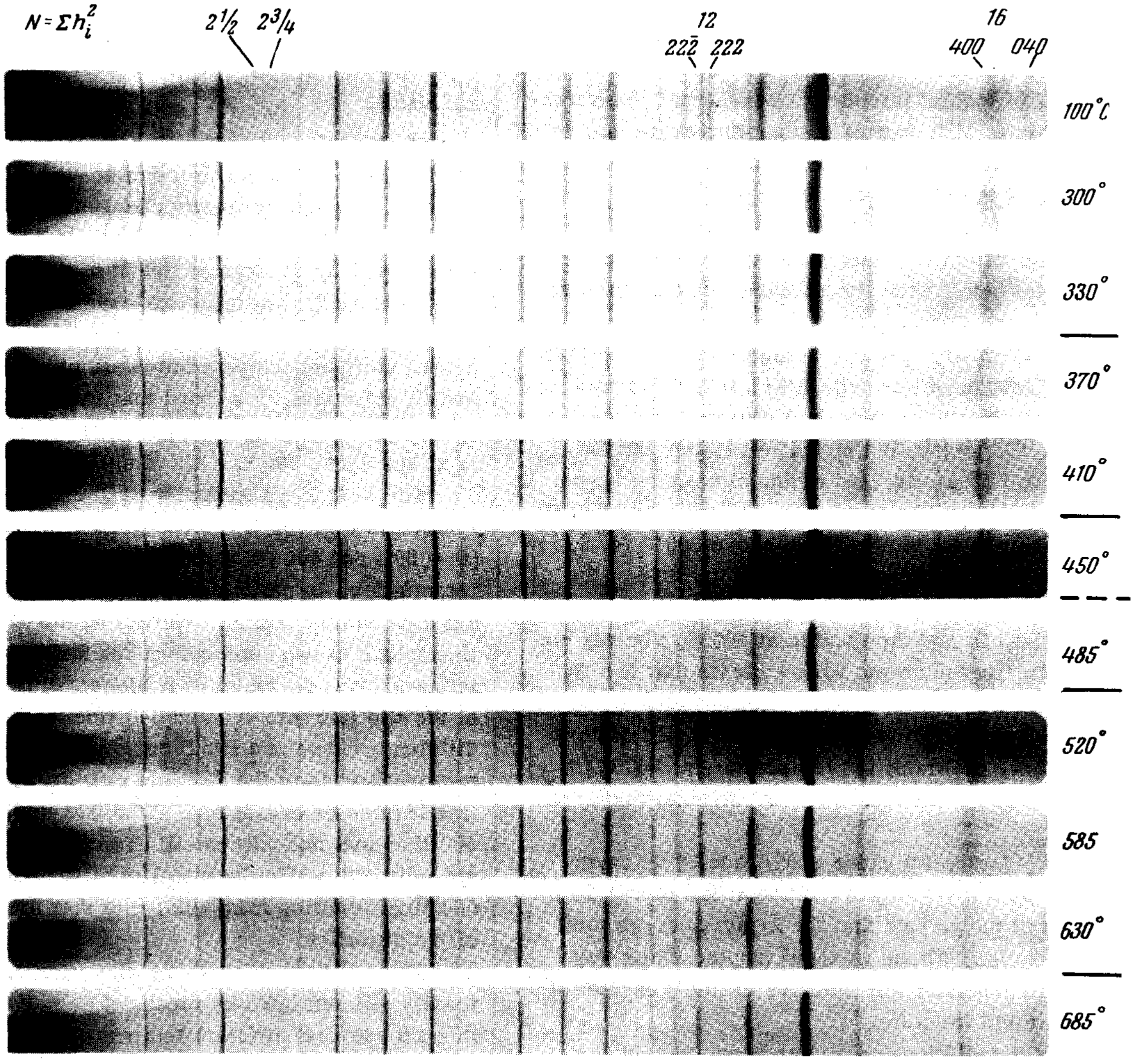

Fig. 1. Patterns recorded from $NaNbO_3$ with Fe radiation at several temperatures. The temperature ranges covering phase transitions are indicated by lines.

method was applied for the tetragonal and cubic cells; the 400 lines alone were used and gave $\Delta a = \Delta c = \pm 0.0006$A; $\Delta v = \pm 0.03 A^3$.

Results

The $NaNbO_3$ was found to have the same line splitting at room temperature and at -196°C (Cu radiation was used). This means that the structure is unchanged, so $NaNbO_3$ has no phase transitions in this range.

Figure 1 shows typical patterns recorded with Fe radiation at up to 700°C. The perovskite-type structure is retained throughout, but the splittings (especially of the 222 and 400 lines) indicate that the subcell undergoes a number of minor changes. (The black spots and extra lines at small angles are technical defects; they are unrelated to these effects).

The splittings in the 222 and 400 lines at temperatures up to 360°C are typical of pseudomonoclinic distortion; $a = c \neq b$, $\beta > 90°$. The true symmetry of $NaNbO_3$ in that range is orthorhombic, in accordance with earlier results.

The splitting of 400 is lost at about 360°C, but there is a persistent splitting of 222 characteristic of monoclinic distortion; the monoclinic subcell has parameters $a = b = c$, $\beta > 90°$, which means that $NaNbO_3$ remains orthorhombic.

All lines, including 222, lose their splittings between about 430°C and about 520°C; the subcell is to be reckoned as cubic in that range.

The splitting of 400 reappears about 520°C, but this time it is characteristic of a tetragonal subcell with $c/a > 1$. The 222 line is not split. The splitting of 400 increases up to 500°C, but thereafter decreases; it vanishes at about 640°C, and the subcell is then cubic.

These results show that transitions occur at 360, 430, 520, and 640°C; but the subcell parameters point also to another at 470°C, which is easily missed if patterns are recorded only at intervals of 30°C. The Table and Fig. 2 give these results; the circles in Fig. 2 indicate the extent of the error, except in the case of β, for which the lines do the same.

Figure 2 shows that all transitions are accompanied either by stepwise changes in the lattice constants (as at 360, 470, and 520°C) or by changes in the temperature coefficients (as at 430 and 640°C). The transition at 360°C involves stepwise reductions in $\underline{a}$ and the subcell volume only; β changes smoothly from 90°40' at room temperature to 90°00' near 430°C.

All the same, the width of the 400 line above 360°C is greater than that for cubic $NaNbO_3$ above 640°C (Fig. 1); this obvious broading in 400 persists up to 520°C. The reason is that the $\underline{a}$ and $\underline{b}$ of the pseudomonoclinic subcell are not exactly equal at 360-430°C; the difference is less than 0.1%, which we took as zero in the calculations. Further, the broadening of 400 at 430-520°C is evidence for similar slight distortion (< 0.1%), although we took the subcell to be cubic. The 222 line is not split at any point within this range, so the distortion cannot be of monoclinic type; the broadening of 400 rules out rhombohedral distortion, so the distortion at 430-520°C must be of tetragonal type.

Patterns were recorded at 450 and 500°C with Cr radiation in order to establish the type of change at 470°C. The 321 β-lines ($\theta \sim 80°$) were very broad, which is evidence for a small (< 0.1%) distortion at 430-520°C; but the distortion is too small to be measured or even to be determined as to type. A general analysis of the patterns recorded between 450 and 500°C

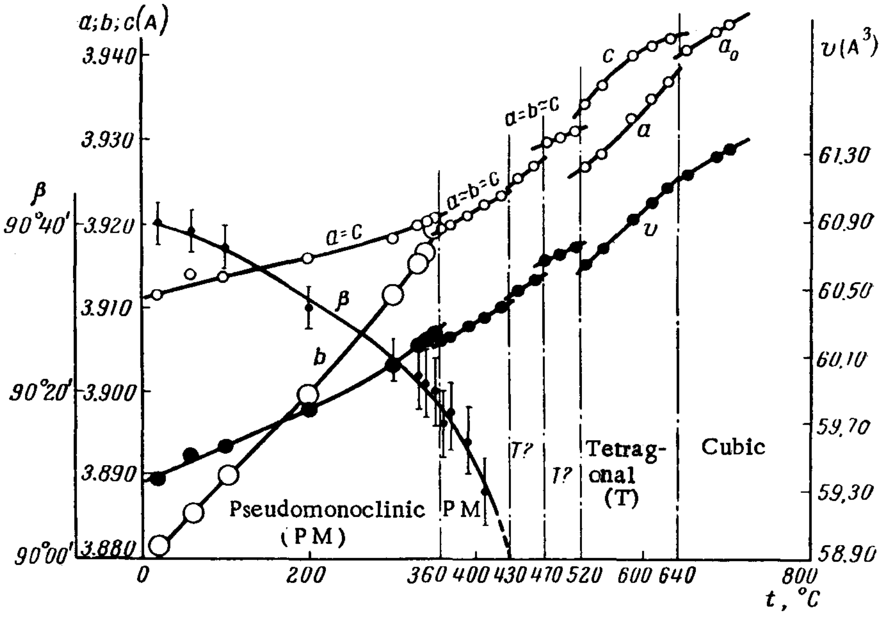

Fig. 2. Subcell parameters of sodium niobate as functions of temperature.

Symmetry and Subcell Parameters of $NaNbO_3$

Temperature, °C	Lattice Parameters				
	Pseudomonoclinic				
	a, A	b, A	β	b/a	v, A^3
−196	3.909_2	3.871_3	90°45′	0.990_1	59.1_7
20	3.911_4	3.881_3	90°40′	0.992_3	59.3_8
60	3.914_1	3.885_4	90°39′	0.992_7	59.5_2
100	3.913_5	3.890_4	90°37′	0.994_1	59.5_8
200	3.915_8	3.899_5	90°30′	0.995_8	59.7_9
300	3.918_1	3.911_5	90°24′	0.998_3	60.0_5
330	3.919_9	3.915_3	90°22′	0.998_8	60.1_6
340	3.920_1	3.916_6	90°21′	0.999_1	60.1_9
350	3.920_7	3.919_3	90°20′	0.999_7	60.2_5
	Pseudomonoclinic				
360	3.919_3	3.919_3	90°16′	1.000	60.2_0
370	3.919_6	3.919_6	90°18′	1.000	60.2_2
390	3.921_0	3.921_0	90°14′	1.000	60.2_8
410	3.922_3	3.922_3	90°08′	1.000	60.3_4
430	3.923_4	3.923_4	<90°08′	1.000	60.3_9
	Pseudocubic				
	a, A				
450	3.925_4				60.4_9
470	3.926_8				60.5_5
	Pseudocubic				
485	3.929_6				60.6_8
500	3.930_1				60.7_0
520	3.931_1				60.7_5
	Tetragonal				
	a, A	c, A		c/a	
530	3.926_7	3.934_1		1.001_9	60.6_6
550	3.928_2	3.936_4		1.002_1	60.7_4
585	3.932_6	3.940_0		1.001_9	60.9_3
610	3.934_8	3.941_1		1.001_6	61.0_2
630	8.936_8	3.941_8		1.001_3	61.0_9
	Cubic				
	a, A				
650	3.940_4				61.1_8
685	3.942_8				61.2_9
700	3.943_6				61.3_3

revealed no certain differences. The symmetry for this range is shown as doubtfully tetragonal in Fig. 2.

A further feature so far neglected is that all patterns recorded at up to 600°C show superlattice lines whose strengths decrease as 600°C is approached; they become scarcely detectable at that temperature. The lines seen best are those whose parameters, squared, give sums N of $2^1/_2$ and $2^3/_4$, which Wood [4] ascribes to doubling of a and c, and quadrupling of b, for the pseudomonoclinic subcell at room temperature. We have made no special study of these effects, but these lines showed no very great change in position or relative intensity within the temperature range used.

Discussion

Our results show that $NaNbO_3$ has phase transitions at about 360, 430, 470, 520, and 640°C. Four of these (those at 360, 470, 520, and 640°C) have been reported before [9, 10]; the temperatures are confirmed.

The second-order transition at 430°C has not been reported before; the x-ray results indicate that $NaNbO_3$ is orthorhombic between 360 and 430°C, so there is no longer any conflict between the x-ray and optical data for temperatures above 360°C.

The small monoclinic distortion at 360-430°C ($a = c \cong b$, $\beta > 90°$), as detected with Cu radiation, gives precisely the splitting of 422 line to be expected for the tetragonal distortion. This would explain the erroneous conclusions that have been drawn [4, 9, 11].

The superlattice lines show no marked variation, so we may assume that the supercell is 16 unit cells no matter what the transition (including the one at 430°C). The last result is to be expected, because the pseudomonoclinic subcell becomes pseudocubic in a continuous fashion as β falls gradually to 90°. If we take the subcell to be cubic above 430°C, the true symmetry must change from orthorhombic to tetragonal at that temperature. Below 430°C the pseudomonoclinic subcell has $a = c = b$, $\beta > 90°$, and above 430°C $a = c = b$, $\beta = 90°$; so above 430°C $NaNbO_3$ has $c'/a' = 4b/2a = 2$, although the supercell is still $2 \times 2 \times 4 = 16$. The slight distortion between 430 and 520°C appears to be of tetragonal type, but we no longer have $c'/a' = 2$ precisely. However, this leaves undecided the differences between the tetragonal phases found above 430, 470, and 520°C.

Tetragonal $NaNbO_3$ becomes orthorhombic on cooling, but at 430°C, not at 360°C as claimed previously [4, 9, 11]; the transitions starts with a gradual increase in β. Near 360°C, when $\beta = 90°16'$, there is a discontinuous change in the $\underline{a}$ of the subcell; this is the sole result of the spontaneous deformation associated with the sharp rise in the dielectric constant of $NaNbO_3$ at 360°C. In fact, $NaNbO_3$, is a good example of an antiferroelectric in which the structure change responsible for that behavior may be differentiated from the deformation of the O−Nb−O angles (changes in the B−O chains [15]).

This is very important, because it is believed [5] that the NbO_6 octahedra are very much distorted by the displacement of the Nb atoms (the Nb−O bonds are deformed). The wide splitting of the 400 lines at temperatures up to 360°C (in the antiferroelectric range) is a direct result of this distortion and displacement, while the superlattice effects are very small subcell distortions above 360°C are caused by the deformation, which is not associated with any definite anomaly in the dielectric constant or with large distortions in the NbO_6 octahedra.

The distortion of the BO_6 octahedra is associated with antiferroelectric (and ferroelectric) behavior in other compounds of ABO_3 type, e.g., in $PbZrO_3$ [16]. All the same, some ABO_3 compounds that resemble $NaNbO_3$ and $PbZrO_3$ in having geometrical factors $t < 1$ (e.g., $CaTiO_3$ [17], $NaTaO_3$ [18], etc.) do not resemble those compounds in their properties at room temperature; they contain undistorted BO_6 octahedra. This fact has led us to assume [19, 20] that ABO_3 compounds having the perovskite structure and having $t < 1$ (in which the B−O chains alter) have a necessary (but not sufficient) precondition for antiferroelectric behavior. The sufficient condition is that the chains must have a critical degree of kinking adequate to distort the BO_6 octahedra and so to make it possible for the caged B atoms to move; this degree varies from one compound to another.

That degree for $NaNbO_3$ is reached only at 360°C; the transitions at 430, 470, 520, and 640°C correspond to deformations in the valence angles such that the BO_6 octahedra are not rendered irregular.

Our results show that a proper choice of x-ray technique can provide an adequately sensitive method of detecting small distortions in the unit cell.

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