configuration, and that the intramolecular chlorine–chlorine distance is 4·24 ± 0·04 A.

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A Study of the Unit-cell Dimensions and Symmetry of certain Ferroelectric Compounds of Niobium and Tantalum at Room Temperature

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An account is given of the methods of preparation of the recently reported ferroelectric compounds $KTaO_3$, $KNbO_3$, $NaNbO_3$ and $NaTaO_3$, and of an investigation of their structure from powder photographs. At room temperature $KTaO_3$ is cubic and the other compounds orthorhombic, the distortion from the simple perovskite structure being similar to that which $BaTiO_3$ shows between − 5 and 90° C. From an examination of the variation of Curie point with lattice parameter of these compounds, it is suggested that the factor primarily responsible for the ferroelectricity is the degree of homopolar bonding of the tantalum, niobium or titanium ion with the oxygen ion.

Introduction

In a recent note Matthias (1949) reported that the niobates and tantalates of sodium and potassium, which are pseudo-isomorphous with $BaTiO_3$, exhibit ferroelectric properties. These salts gave a piezoelectric response and showed dielectric hysteresis loops, with peaks in their dielectric constant versus temperature curve corresponding to changes in crystal symmetry. These changes in symmetry were observed by studying crystals, of 1–2 mm. cube edge, with the polarizing microscope. The room-temperature symmetry of the compounds was given as pseudo-tetragonal from a study of the X-ray powder photographs, with an axial ratio of $\simeq 0{\cdot}99$ for the niobates, and rather closer to unity for the tantalates. The observations described below, which have been previously briefly reported (Vousden, 1951), were undertaken in order to make accurate determinations of the unit-cell dimensions of these compounds.

Crystallization of the substances

The compounds were produced as small crystals, of volume of the order of 10^{-10} cm.^{3}, from the oxides of tantalum and niobium, of purity 99 and 99·7 % respectively. No chemical analysis of the products was undertaken, but the constancy of the parameters of the same materials prepared under different conditions, or in some cases by different methods, suggested that the effect of any impurity content was negligible.

$NaNbO_3$

A suspension of Nb_2O_5 in NaOH was boiled for about 20 min., and the precipitate, consisting of very small crystals of linear dimensions less than 10^{-4} cm., was filtered and then dried at about 400° C. The powder photograph of the product showed the symmetry of the structure to be cubic, but the line broadening showed the existence of considerable lattice strain. Annealing the compound at about 1100° C. improved the diffraction pattern so that the groups of lines corresponding to the pseudocubic distortion were clearly resolved.

$KNbO_3$

Equimolecular proportions of KOH and Nb_2O_5 were fused at 400° C. in a platinum crucible. The resulting product, consisting of a white crystalline powder, was then reground and reheated to the same temperature several times in order that the reaction might be more

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complete. The diffraction lines of the powder photograph of the final product were very well resolved. If excess KOH was used in the preparation, or if the product was heated to above 1000° C., the colour of the compound changed from white to dark grey. No new lines appeared on the powder photograph, and no noticeable change of cell parameters accompanied this change, but the background intensity increased and the resolution of the diffraction lines decreased.

$KTaO_3$ *and* $NaTaO_3$

These were prepared by the method described in the papers referred to in Mellor's *Inorganic Chemistry*. The orthohexatantalate was first produced by fusion of Ta_2O_5 with KOH or NaOH, and then the resultant product was recrystallized from water, calcined, and annealed at 1000° C.

Analysis of the X-ray diffraction powder photographs

The powder photographs used for the structure determinations were taken with Cu $K\alpha$ radiation, and were obtained from samples which gave best resolution of the diffraction lines. The line broadening caused by geometrical factors was reduced as much as possible by the use of thin straight specimens, of diameter 0·1–0·2 mm., rolled with gum tragacanth. These were carefully centred in a 19 cm. diameter camera whose entrance collimating slit was reduced to about 0·2 mm. With these precautions the Cu $K\alpha$ doublet could be resolved at $\theta=40°$ in the photographs of $NaNbO_3$ and $KNbO_3$.

Inspection of the powder photograph of $KTaO_3$ showed that its symmetry was cubic, but the density of lines in the photographs of the other compounds showed their symmetry to be orthorhombic, and not tetragonal as Matthias had reported. An optical examination of the crystals of these compounds in polarized light showed that, though of cubic habit, they gave straight and symmetrical extinction, similar to that of $BaTiO_3$ in the orthorhombic phase (Forsbergh, 1949; Kay & Vousden, 1949). That the type of distortion was in fact the same as in $BaTiO_3$ was shown by an examination of the 400, 220 and 222 groups of reflexions. The distortion is derived from a cubic unit cell by a small shear of one of the (100) faces and a small contraction of the cube in a direction perpendicular to this face. The symmetry of the original cube now becomes monoclinic, but if two new axes are chosen in the sheared cube face, which bisect the angle between the two equal axes of this monoclinic cell, the symmetry of the unit cell defined by these axes is orthorhombic. The third axis, parallel to one edge of the original cube, retains the same direction.

Method of indexing

The diffraction lines of the powder photograph are all grouped around the positions of those lines which would be obtained from a cubic structure with the same average lattice parameter. At high orders the groups begin to overlap, but for low orders it is obvious to which group any given line belongs. This leads to a convenient method of indexing, for the axial lengths may be expressed in the form

$$a=\sqrt{2}\,b(1+\delta_1),\quad c=\sqrt{2}\,b(1+\delta_2).$$

Where δ_1 and δ_2 are small quantities, and a, c are the longer and shorter axes respectively of the orthorhombic cell, which bisect the angle between the two equal monoclinic axes (a', c') nearly parallel to the two axes of the cubic cell. The b axis is parallel to the other cube axis.

Neglecting terms in δ_1^2 and δ_2^2, expansion of the expression for the spacing corresponding to the hkl reflexions (d_{hkl}) gives

$$d_{hkl}=\frac{b}{n}(1+\tfrac{1}{2}h^2\delta_1+\tfrac{1}{2}l^2\delta_2)=\frac{b}{n}(1+\delta), \tag{1}$$

where the indices are referred to the orthorhombic cell and $n^2=h^2+k^2+l^2$.

Approximate values of δ_1 and δ_2 may be obtained from the splitting of the low-order groups of diffraction lines, whose indices are obvious from inspection if the lines are well resolved. From these approximate values a table of values of $(b/n)(1+\delta)$ may be constructed for higher orders. The spacings of these high-order diffraction lines are now calculated from their measured positions on the films. The value of $b\delta/n$ is subtracted from these values, and if the indexing is correct the remainder, divided by n, should be constant and equal to b. The value of b obtained will in general vary slightly with h and l because the values of δ_1 and δ_2 are approximate, and from an examination of this variation more accurate values of δ_1 and δ_2 may be chosen until the variation of b is within the random error. Alternatively, the axial lengths may be calculated directly from the high-order lines. The most accurate value of b is then obtained by plotting the values obtained against $\cos^2\theta$, and extrapolating the result to $\theta=90°$ in the usual way. The table of values of $b(1+\delta)/n$ can include those of the α_1 and α_2 components, and any overlapping of reflexions will be immediately shown. By this method the indexing of all lines may be rapidly carried out and the absence of any reflexions revealed.

Results

The number of high-order reflexions indexed varied from twenty to forty in the different compounds. The final parameters are given in Table 1, together with the degree of distortion from cubic symmetry, which is expressed in terms of the shear of the cube face ($\delta\theta$) and of the contraction of the perpendicular axis (δs), which are equal to $(\delta_1-\delta_2)$ and $\frac{1}{2}(\delta_1+\delta_2)$ respectively. The comparable values for $BaTiO_3$ at −10° C. are also given. The order of accuracy of the parameters of $NaNbO_3$ and $KNbO_3$ is $\pm 0{\cdot}01\,\%$, of $KTaO_3$ is $\pm 0{\cdot}003\,\%$, and of $NaTaO_3$ is $\pm 0{\cdot}02\,\%$. The constant calibration angle subtended by the knife edges of the camera was measured to ±0·002 % on an accurate goniometer table, preliminary experiments having suggested that the parameters of quartz, usually taken as a calibration standard, were insufficiently reproducible for the purpose (see Keith, 1950). The ultimate error limiting the accuracy of the results was that of film measurement, which error varied from ±0·002 to ±0·004 cm.

Temperature changes in $NaNbO_3$ *crystals*

The birefringence of $NaNbO_3$ crystals, which is of the order of 0·1 at room temperature, decreased on heating until at about 300° C. the symmetry changed to tetragonal. At about 600° C. another phase transition occurred and the crystals became cubic and isotropic. No change in symmetry occurred if the crystals were cooled to a temperature $-173°$ C., so that the orthorhombic phase, which in $BaTiO_3$ exists over a range of 85° C., is stable in $NaNbO_3$ over a temperature range exceeding 500° C. This result suggests in fact that the rhombohedral phase does not occur at any temperature in $NaNbO_3$, whereas in $BaTiO_3$ the symmetry is rhombohedral below $-90°$ C.

Discussion of results

The ideal perovskite structure with cubic symmetry has the general formula ABO_3, where A, B, are metallic ions of ionic radii $R_A \sim 1{\cdot}2$ A. and $R_B \sim 0{\cdot}6$ A. respectively. The B and A ions occupy the centres and corners of the unit cell respectively, while the oxygen ions occupy the face centres. The important interionic distances are thus A–O and B–O, equal to $R_A + R_O$ and $R_B + R_O$ respectively, where R_O is the radius of the oxygen ion.

From the values of the parameters given in Table 1, together with the values of the Goldschmidt radii of the ions, corrected for co-ordination number, a comparison may be made between the observed bond lengths and the ideal values obtained from the ionic radii. This comparison is shown in Table 2, together with the value of t, a tolerance factor first introduced by Goldschmidt (1926*a*, *b*). This factor is given by

$$R_A + R_O = \sqrt{2}\, t(R_B + R_O),$$

and is thus a measure of the ion misfit in the structure.

From an empirical study of the lattice parameters of several compounds having the perovskite, or pseudo-perovskite, structure, Megaw (1946) has shown that the cubic structure results only if $0{\cdot}9 < t < 0{\cdot}97$. If $0{\cdot}8 < t < 0{\cdot}9$ the symmetry is distorted to orthorhombic, while if $0{\cdot}97 < t < 1{\cdot}02$ a slight tetragonal distortion results. If $0{\cdot}8 > t > 1{\cdot}02$ an entirely different crystal structure results. Of the barium, strontium and calcium titanates only $BaTiO_3$ is ferroelectric, and it has been generally assumed that this is the result of the increase in the freedom of movement of the titanium ions arising from the increase in the B–O distance, due to the large radius of the barium ion (e.g. Rushman & Strivens, 1946). Thus as strontium replaces barium in the lattice the Curie point decreases. However, this large change in Curie point with parameter is not shown by the niobate ferroelectric compounds, for Table 2 shows that, though the change of t between $NaNbO_3$ and $KNbO_3$ is as large as the change between $BaTiO_3$ and $CaTiO_3$, both the niobium compounds are ferroelectric. Their Curie points are in fact of the same order of magnitude. To add to this inconsistency, whereas the transition point of pure $KTaO_3$ has recently been reported at 13·2° K. (Hulm, Matthias & Long, 1950) that of $NaTaO_3$ is higher than room temperature, giving a dependence of Curie point on parameter in these compounds exactly opposite to that of the barium–strontium series. Moreover, any suggestion that the Curie point is determined mainly by the total electronic polarizability of these compounds (e.g. Roberts, 1949) is contradicted by the fact that the total electronic polarizability of $KTaO_3$ is higher than that of $NaTaO_3$ while its Curie point is very much lower.

These observations clearly show that the Curie point is determined by some other factor in the structure which varies considerably with the nature of the B ion,

Table 1. *Final parameters*

Material	Symmetry	$\delta\theta$	$\delta s = a'/b$	a (A.)	c (A.)	b (A.)
$KTaO_3$	Cubic	—	—	3·9885	3·9885	3·9885
$NaTaO_3$	Orthorhombic	29·0′	1·0017	5·5239	5·4778	3·8831
$KNbO_3$	Orthorhombic	15·8′	1·0162	5·7203	5·6946	3·9714
$NaNbO_3$	Orthorhombic	40·2′	1·0091	5·5682	5·5052	3·8795
$BaTiO_3$ (−10° C.)	Orthorhombic	8·4′	1·0058	5·682	5·669	3·990

Table 2. *Comparison between observed bond lengths and ideal values*

Compound	$R_B + R_O$ ($R_O = 1{\cdot}32$ A.) (A.)	B–O (A.)	Difference (A.)	$R_A + R_O$ ($R_O = 1{\cdot}32$ A.) (A.)	A–O (A.)	Difference (A.)	t
$NaNbO_3$	2·01	1·95	−0·06	2·37	2·76	+0·39	0·83
$NaTaO_3$	1·99	1·93	−0·06	2·37	2·72	+0·35	0·84
$KNbO_3$	2·01	2·00	−0·01	2·74	2·82	+0·08	0·97
$KTaO_3$	1·99	1·99	−0·00	2·74	2·81	+0·07	0·98
$CaTiO_3$	1·96	1·90	−0·06	2·45	2·68	+0·23	0·89
$SrTiO_3$	1·96	1·95	+0·01	2·68	2·76	+0·08	0·97
$BaTiO_3$	1·96	2·00	+0·04	2·84	2·82	−0·02	1·03

but which, for the same B ion, may vary with the lattice spacing in a fairly regular manner. The only quantity which seems likely to cause such effect is the presence of homopolar bonding between the B and oxygen ions. Such a suggestion has frequently been made (e.g. Eucken & Büchner, 1934; Megaw, 1947), but it has not been considered that the ferroelectricity depends primarily on the existence of such bonding, as these results suggest. The proportion of homopolar to ionic bonding would vary considerably for different ions, but if the A ion only is substituted in the structure a correlation between lattice spacing and change in Curie point might be expected. The experimental results require the ratio of change of Curie point with lattice parameter, to be positive, negative, and about zero in the titanates, tantalates, and niobates respectively.

On the other hand, the relation

$$\delta\theta \propto (1{\cdot}5 - R_A) \qquad (2)$$

holds within about 20 % for all compounds in Table 2 with orthorhombic symmetry, and also for $CaTiO_3$, which is not ferroelectric. Such a result has a reasonable interpretation if it is assumed that the internal stresses producing the shear in the different compounds are approximately the same, and are independent of temperature. The shear involves a change in the A–O, but not the B–O bond lengths, so that the restoring forces may be expected to be roughly of the form

$$1/\{(A\text{–O}) - (R_A + R_O)\},$$

reaching infinity when the ions are touching and $t=1$. This will lead to a relation of type (2).

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Short Communications

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The crystal structure of salicylic acid.

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Salicylic acid provides one of the best examples of a substance whose physical and chemical properties indicate hydrogen-bond formation between the hydroxyl group and an adjacent oxygen atom of the same molecule. The crystal structure of this compound has been determined from a study of the Patterson function projected on the (001) and (010) planes, and of the Fourier transform of a single molecule.

The optical and morphological properties of the crystals are described by Groth (1906–19, vol. 4, pp. 453, 493). X-ray measurements show

$$a = 11{\cdot}5_2,\ b = 11{\cdot}2_1,\ c = 4{\cdot}90 \text{ A.},\ \beta = 91°.$$

The space group is $P2_1/a$. Fig. 1 shows the electron density projected on the (001) plane. The corresponding $F(hk0)$'s were measured using a Geiger-counter spectrometer, and the value of $\Sigma \mid F_o - F_c \mid \div \Sigma \mid F_o \mid$ is 0·12 at the present stage of refinement.

The association of two molecules through their carboxyl groups can be clearly seen from this projection. It is known that salicylic acid forms dimers in solvents such as benzene. $(F_o - F_c)$ syntheses lead to the following conclusions. The hydrogen atoms in the 3, 4, 5 and 6 positions are represented by electron-density maxima† of about 0·8 e.A.$^{-2}$; the position of a similar maximum close to the oxygen of the hydroxyl group is consistent with an O–H

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† These maxima cannot be distinguished in the projection reproduced in Fig. 1.