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Structural and Electrical Properties of Silver Niobate and Silver Tantalate*

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At room temperature both $AgNbO_3$ and $AgTaO_3$ possess orthorhombic multiple-cell perovskite-type structures and are isomorphous with $NaNbO_3$. In $AgNbO_3$ the structure changes sharply to near-tetragonal at 325° C., while in $AgTaO_3$ a similar change occurs, more smoothly, at about 375° C. At higher temperatures a sequence of structural changes closely similar to that in $NaNbO_3$ leads to a fully isotropic condition at 560° C. for $AgNbO_3$ and 480° C. for $AgTaO_3$.

The permittivity of $AgNbO_3$ shows a peak at the orthorhombic–tetragonal transition reminiscent of that normally observed at a ferroelectric or antiferroelectric Curie temperature. Weak hysteresis and pyroelectric effects indicate a low value of spontaneous polarization. It is concluded that in $AgNbO_3$ the structural changes are probably influenced chiefly by ionic packing considerations. With $AgTaO_3$ the presence of free silver precluded electrical measurements, but the nature of its structure transitions and the permittivity data obtained for the solid solution $AgNb_{0.75}Ta_{0.25}O_3$ suggest the absence of ferroelectricity.

1. Introduction

A number of perovskite-type niobates and tantalates are known to possess distorted pseudo-cubic structures and to undergo structure changes with temperature, some of which are associated with transitions from the ferroelectric or antiferroelectric to the paraelectric state.

Shirane, Newnham & Pepinsky (1954) have studied ferroelectric $KNbO_3$ and find that its structural and electrical properties are closely similar to those of $BaTiO_3$. $NaNbO_3$ differs from $KNbO_3$ in that it is antiferroelectric with a multiple-type pseudo-cubic perovskite structure cell possessing monoclinic symmetry. The structure has been described as 'puckered' by Megaw (1952) because both the Na and Nb ions are slightly displaced from their special positions in the crystal lattice (Vousden, 1951).

Detailed high-temperature X-ray powder studies of $NaNbO_3$ have been made by Wood (1951), Shirane *et al.* (1954), and Francombe (1956). It has been shown that the structure changes discontinuously from orthorhombic to pseudo-tetragonal at the Curie temperature, 360° C. At temperatures above 500° C., the puckering of the structure is gradually eliminated and a monomolecular cubic structure cell is assumed at 640° C.

During a general exploration of compositions of the $A^{+1}B^{+5}O_3$ type, it was discovered that the compounds $AgNbO_3$ and $AgTaO_3$ could be prepared, and that these possessed pseudo-cubic perovskite-type structures apparently isomorphous with that of $NaNbO_3$. The purpose of this paper is to present the results of electrical and X-ray studies of these two silver compounds, and electrical data for the solid solution $AgNb_{0.75}Ta_{0.25}O_3$.

2. Preparation of specimens

Disc-shaped ceramic samples of $AgNbO_3$, $AgTaO_3$ and their solid solutions were prepared by pressing, and firing, mixtures of Ag_2O with the appropriate pentoxide or with mixtures of Nb_2O_5 and Ta_2O_5 prefired at 1200° C. All firings of the pressed discs were carried out in air at temperatures between 1000 and 1100° C. If higher firing temperatures are employed, decomposition and loss of silver occurs. Electrodes were applied to the faces of the discs so that electrical measurements could be made.

Specimens used in electrical studies were subsequently powdered into a form suitable for X-ray examination and were heat-treated at 900° C. to remove strain effects. X-ray powder photographs for such products in general showed well-resolved high-angle diffraction lines.

3. X-ray examination

X-ray powder studies were made between 20° C. and 700° C., using a Unicam 19 cm. high-temperature camera with Cu $K\alpha$ radiation. Calculations of monoclinic unit-cell parameters were based on measurements of high-angle diffraction line groups with Σh^2 values (referred to the pseudo-cubic perovskite structure) of 22 and 24.

X-ray powder patterns of $AgNbO_3$ and $AgTaO_3$ at room temperature closely resemble that of $NaNbO_3$, and indicate that the structures are isomorphous. In particular, the superlattice effects appearing on the X-ray pattern of $AgNbO_3$ are very similar to, but weaker than, those found with $NaNbO_3$. This suggests

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that the multiplicity of structure-cell dimensions is the same in both structures. Superlattice effects could not be positively detected with $AgTaO_3$, and it is concluded that any ionic displacements from ideal sites are appreciably smaller than, or different in type from, those in $NaNbO_3$.

Lattice parameters calculated for the pseudo-cubic, monoclinic unit cell at 20° C. are

$AgNbO_3$: $a_0 = c_0 = 2\times3{\cdot}944$, $b_0 = 4\times3{\cdot}915$ Å, $\beta = 90° 34'$.
$AgTaO_3$: $a_0 = c_0 = 3{\cdot}931$, $b_0 = 3{\cdot}914$ Å, $\beta = 90° 21'$.

Values of unit-cell dimensions obtained in the same way for $NaNbO_3$ (Francombe, 1956) are

$NaNbO_3$: $a_0 = c_0 = 2\times3{\cdot}914$, $b_0 = 4\times3{\cdot}881$ Å, $\beta = 90° 39'$.

The changes shown in the structures of both $AgNbO_3$ and $AgTaO_3$ at higher temperatures are strikingly similar to those occurring in $NaNbO_3$. Thus, as the temperature is increased, X-ray diffraction-line splitting is gradually reduced; in each instance the dimensions of the monoclinic simple perovskite-type unit cell approach a common value and the angle β decreases. In both $AgNbO_3$ and $AgTaO_3$ the first transition in each substance corresponds to an almost complete disappearance of the line splitting. In $AgNbO_3$ this occurs comparatively suddenly at about 325° C., while in $AgTaO_3$ the change is gradual and line splitting appears to reach a minimum at about 370° C. Lattice parameters (referred to the pseudo-cubic unit cell) as a function of temperature are shown in Fig. 1. The behaviour of the two substances at the transition temperature can best be compared by referring to the change in the monoclinic β parameter, the discontinuous nature of which is more marked for $AgNbO_3$ than for $AgTaO_3$.

With each substance the small amount of relative line broadening which remains just above the transition temperature indicates a slight tetragonal or pseudo-tetragonal distortion of the simple perovskite-type unit cell. For $AgNbO_3$, however, weak superlattice effects are still present which indicate that the multiplicity of the unit-cell dimensions existing at room temperature persists in the tetragonal range, and the structure should not therefore be described as 'near-cubic'. As the temperature is further raised the tetragonal-type diffraction-line splitting increases to a maximum and then decreases, disappearing completely at about 550° C. for $AgNbO_3$ and at about 485° C. for $AgTaO_3$. The superlattice effects for $AgNbO_3$ are no longer detectable above 550° C., and for both substances the structure above these upper transition temperatures has become strictly cubic, with a simple monomolecular unit cell. The whole sequence of changes is very similar to that observed in $NaNbO_3$, except that the magnitude of the change of lattice parameters at the orthorhombic–tetragonal transition temperature is less, and that a gradual decrease of tetragonal-type line splitting immediately above this temperature (Shirane *et al.*, 1954) is not shown by $AgNbO_3$ and $AgTaO_3$.

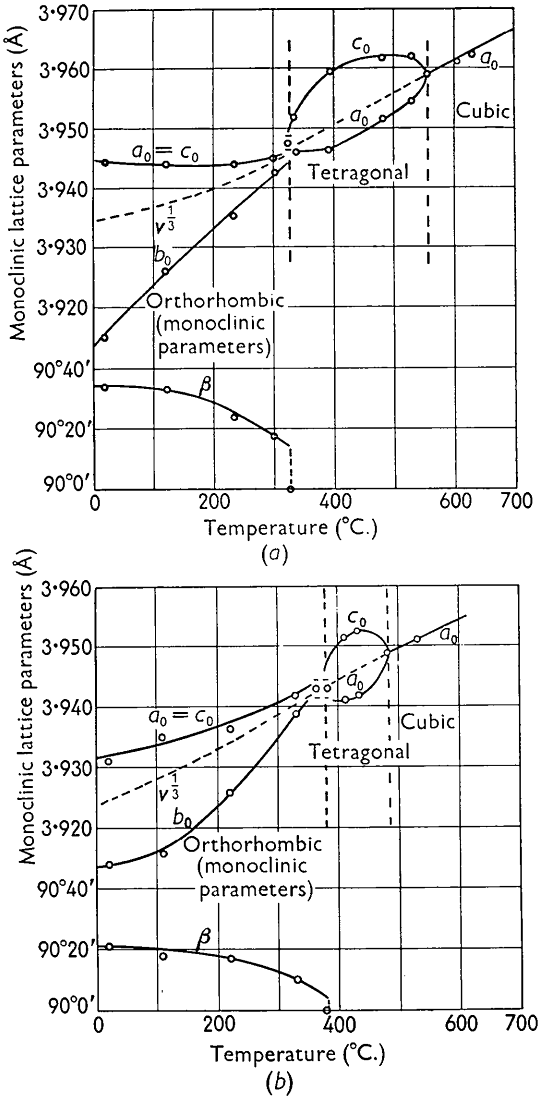

Fig. 1. Lattice parameters (*a*) of $AgNbO_3$, (*b*) of $AgTaO_3$.

4. Electrical properties

Electrical measurements were made on samples of $AgNbO_3$ and a solid solution of composition $AgNb_{0{\cdot}75}Ta_{0{\cdot}25}O_3$. Specimens of $AgTaO_3$ and $AgNb_{0{\cdot}5}Ta_{0{\cdot}5}O_3$ invariably contained free silver and were highly conducting. Consequently no permittivity values could be obtained for these specimens.

The permittivity–temperature curve for $AgNbO_3$, obtained by bridge measurements at 500 kc.sec.$^{-1}$, has sharp maxima at 60° C. and at 340° C., as shown in Fig. 2(*a*). The first maximum is small and is not

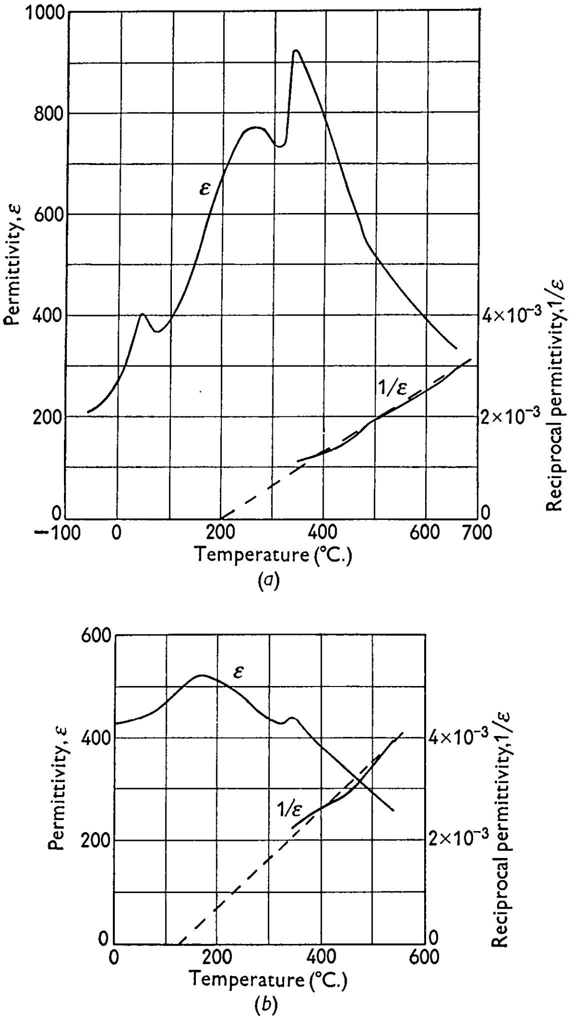

Fig. 2. Permittivity-temperature curves (*a*) for $AgNbO_3$, (*b*) for $AgNb_{0\cdot75}Ta_{0\cdot25}O_3$.

associated with any observed change in crystal structure. The peak at 340° C., however, corresponds closely to the discontinuous change from orthorhombic to pseudo-tetragonal symmetry, and in this respect is similar to the permittivity peak observed in $NaNbO_3$ at 355° C. (Shirane *et al.*, 1954). A further broad maximum occurs between 200° C. and 300° C. but, as with the anomaly at 60° C., no correlation with structural changes is apparent.

Above 340° C. the permittivity falls off roughly linearly with temperature. There is no indication in the permittivity curve of the final structural transition at 550° C. A plot of $1/\varepsilon$ against T shows that the asymptotic Curie temperature θ, of the Curie–Weiss relation $\varepsilon = C/(T-\theta)$, is substantially lower than the temperature of the maximum of permittivity. For most ferroelectrics and antiferroelectrics these two temperatures are usually quite close to one another, although $NaNbO_3$ is a notable exception. Thus, from the permittivity–temperature data, no firm conclusion can be drawn as to whether or not $AgNbO_3$ is ferroelectric.

The permittivity-temperature curve for $AgNb_{0\cdot75}Ta_{0\cdot25}O_3$, shown in Fig. 2(*b*), is similar to that for $AgNbO_3$, but the values of the permittivity maxima are much lower.

Polarization-field loops for $AgNbO_3$ have been examined using the usual Sawyer & Tower circuit. Most specimens appear to show perfectly linear P–E relations, at 50 c.sec.$^{-1}$, up to the highest fields used, some 30 kV.cm.$^{-1}$. Some non-linearity, however, was observed in a few particularly well-sintered specimens (density 6·2 g.cm.$^{-3}$, compared with the ideal density of 6·75 g.cm.$^{-3}$), showing a perceptible knee at about 10 kV.cm.$^{-1}$ but no saturation of polarization and very low remanent polarization at $E = 0$.

A search for piezoelectric activity, by exciting resonant oscillation in bars or discs, showed no detectable effect, either after poling with a d.c. field of up to 50 kV.cm.$^{-1}$ for several hours, or in the presence of a field of 20 kV.cm.$^{-1}$. An accelerometer test, however, showed very weak activity at the remanent state of polarization.

Another test for the existence of remanent polarization used the pyroelectric effect; the charge appearing on the specimen when its temperature changed suddenly was measured by an electrometer. Measurement of the total charge released by complete thermal depolarization at 350° C. was not possible because of the leakage conductivity of the specimen itself at that temperature. Measurements between room temperature and 150° C. indicated a value of remanent polarization substantially higher than that shown by hysteresis loops, but still very much lower than for $BaTiO_3$-type ferroelectrics.

5. Discussion

The dielectric and structural properties of $AgNbO_3$ show marked differences from those of any other known ferroelectric or antiferroelectric material. The evidence of a small remanent polarization, from hysteresis loops and the pyroelectric effect, indicates weak ferroelectricity and leaves open the possibility of antiferroelectricity. The sharp maximum in the permittivity–temperature curve at 50° C. is not associated with change in the crystal structure and is difficult to explain. Also the extended maximum below the transition temperature is a very unusual feature which is not shown by other ferroelectric or antiferroelectric materials.

In $AgNbO_3$, and probably in $AgTaO_3$ also, the final structural transition, to simple cubic, can be interpreted in terms of the straightening out of puckered Nb–O or Ta–O chains. The puckering arises because the mean lattice spacing is too small to accommodate linear Nb–O or Ta–O chains. Using the Goldschmidt radii, corrected for co-ordination, $Nb^{5+} = Ta^{5+} =$

0·68 Å, O^{2-} = 1·32 Å, the spacing below which puckering can be expected is 4·00 Å. In an examination of the structural transitions of $NaNbO_3$ and its solid solutions with $KNbO_3$, $Cd_{0.5}NbO_3$, and $Pb_{0.5}NbO_3$ (Francombe & Lewis, 1957) it was found that the temperature at which the multiple unit cell becomes single varies with composition from above 800° C. to below room temperature. The lattice spacing at this temperature, which may be called the puckering transition temperature, was in each case found to be close to 3·94 Å. In $AgNbO_3$ and $AgTaO_3$ the corresponding experimental values are 3·96 Å and 3·95 Å, respectively.

Ferroelectric or antiferroelectric effects appear to play only a minor role in the structural transitions of $AgNbO_3$. One criterion by which ferroelectric properties can be judged in the perovskite structures is the discontinuous nature of the Curie-point structure transition. Thus when unit-cell parameters are plotted against temperature, for substances like $BaTiO_3$ cr $KNbO_3$ which are strongly ferroelectric, or $PbZrO_3$ which is antiferroelectric, a very sharp discontinuity is apparent at the Curie temperature. $KNbO_3$ shows a sudden linear distortion of 1·6% at the Curie temperature (Shirane *et al.*, 1954) associated with a spontaneous polarization of 26 μC.cm.$^{-2}$ (Triebwasser & Halpern, 1955). For $AgNbO_3$ the discontinuous change of β from 90° to 90° 15′ at 325° C. corresponds to a linear distortion of 0·2%, and the spontaneous polarization observed is also small.

With $AgTaO_3$ the structure transition at 370° C. is comparatively smooth and this probably indicates the absence of ferroelectricity. In this connection it is notable that the effect of $AgTaO_3$ in solid solution with $AgNbO_3$ is to lower the measured values of permittivity. In $AgTaO_3$ the changes in structure observed at high temperatures probably arise almost entirely from ionic packing effects.

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Atomic Scattering Amplitudes for Electrons

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Some new values of atomic scattering amplitudes for electrons, intended primarily for use in the determination of crystal structures by electron-diffraction techniques, are presented. These new values are expected to be more reliable than previous ones since they are based on improved data, that is on Hartree–Fock or Hartree self-consistent fields rather than on interpolation techniques for the light atoms, and on the Thomas–Fermi–Dirac potential rather than on the Thomas–Fermi potential for the heavy atoms. Particular attention is given to the calculation of values of these scattering amplitudes at zero scattering angle. Some of the many factors which limit the usefulness of the atomic scattering amplitudes derived here are discussed.

Values of the atomic form factor for neutral magnesium were obtained in the course of the present calculations and are given in the Appendix.

Introduction

In the past several years a marked increase in the application of electron-diffraction single-crystal techniques to the determination of crystal structures has taken place (see for example, Cowley, 1953, 1956). Standard techniques of X-ray analyses, such as Patterson and Fourier syntheses, and the comparison of observed and calculated structure amplitudes, have been carried over to electron-diffraction studies and employed with success. In X-ray analyses a knowledge of atomic form factors $f_X(s)$ is essential. Similarly, in such electron-diffraction investigations a knowledge of atomic scattering amplitudes $f(s)$ is essential. It is the purpose of this paper to derive new, more reliable values of $f(s)$ for many of the elements. Particular attention will be given to the calculation of $f(0)$, the quantity analogous to $f_X(0) = Z$. It will become evident that our very limited knowledge of atomic fields