JOURNAL OF MATERIALS SCIENCE 5 (1970) 487-491

Electrical Conductivity of Reduced Barium Titanate Crystals

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The conductivity, Seebeck coefficient and Curie point have been measured in reduced crystals of barium titanate. The results have been interpreted in terms of a polaron hopping model, leading to an estimated mobility of 5×10^{-4} cm^2 V^{-1} sec^{-1} at 300° K, and an activation energy of 0.074 eV. The Curie point falls as a result of reduction, probably due to the formation of oxygen vacancies. The decrease can be correlated with the changes in conductivity through the estimated carrier density.

1. Introduction

Barium titanate has been an important electronic material for some time, as it is ferroelectric at room temperature, with a high dielectric constant. This arises from its tetragonal structure and the details of the positioning of the Ti-ions relative to the oxygen ions. It has a Curie point at 120° C corresponding with a phase change to a cubic structure. In the tetragonal form the lack of symmetry in the structure leads also to piezoelectric properties, and barium titanate ceramics can therefore be used as transducers in a variety of applications.

More recently the electrical conductivity has become of interest, since when barium titanate is reduced or doped to form a semiconductor, there is a large temperature coefficient of resistance over a temperature range near the Curie point [5]. This has technological applications. For these the titanate is usually employed in the form of ceramic. Nevertheless the study of single crystals is important, as it can often give basic information unobtainable with polycrystalline or ceramic material. In particular, the behaviour at the Curie point has been observed and studied in single crystals [13].

The present authors have previously reported [12] some changes in electrical properties of crystals during reduction, and correlated these with the chemical processes studied by Arend *et al* [1]. In the present paper the results of investigating electrical properties during reduction are interpreted in terms of polaron theory.

2. Sample Preparation

Single crystals of $BaTiO_3$ can be grown by a flux melt process as described by Remeika [11]. A charge, for example, of 40 g $BaTiO_3$, 27 mg Fe_2O_3, 100 g anhydrous KF is melted in a platinum crucible in a furnace and held at 1150°C for about 10 h. The temperature is lowered at 13° C h^{-1} until it reaches 950° C. The crucible is then withdrawn and the potassium fluoride (melting point 850° C) is decanted. The crucible is returned to the furnace and cooled slowly to room temperature. This procedure leads to the growth from the bottom of the crucible of the well known "butterfly" twins, as studied by de Vries [15]. These provide single crystals in the form of thin triangular plates. The *c*-axis lies in the plane of the plate parallel to one of the shorter sides (see fig. 1). We have grown crystals of this type and carried out measurements of electrical and optical properties. We have also purchased such crystals from the Harshaw Chemical Co. The conductivity of these crystals was raised by reduction in hydrogen. Samples were heated at 800° C in alumina boats in a stream of hydrogen for times between 3 and 15 min, and were cooled in hydrogen to room temperature. A furnace of low heat capacity was used to give the required control of the reduction times.

Contacts to the crystals were made using thermosetting silver or platinum paste. In either case it was necessary to "spark" the contacts after firing by discharging an 0.1 μF condenser

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charged to 800 V. This gave low resistance ohmic contacts.

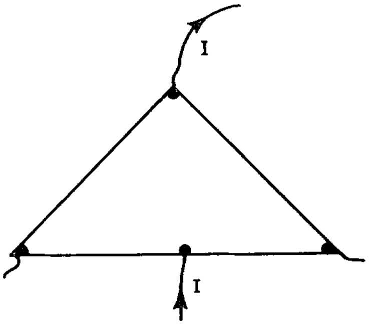

Figure 1 Geometry selected for use in van der Pauw arrangement.

3. Resistivity Measurement

A Van der Pauw method [14] was used for measuring resistivity ρ, and in attempts to measure Hall coefficient. The crystals were very brittle, and no method could be found for cutting samples to the ideal clover-leaf shape. It was necessary, in fact, to use the triangular crystals as grown. Tests were made using graphited paper with silver "dag" electrodes to find which arrangement of contacts gave least error due to finite contact size. It was concluded that the arrangement in fig. 1 was best, and that the contact at the centre of the hypotenuse was the most critical. Plotting equipotentials also showed that the Hall coefficient should be measured with the current flow as indicated; flow from corner to corner gives distortion of equipotentials by the contact at the centre of the hypotenuse.

The resistivity was measured by determining the four cyclic resistances R_{abcd}, R_{bcda}, R_{cdab} and R_{dabc}. These were taken in cyclic pairs and the resistance calculated from the der Pauw formula:

$$\rho = \frac{d(R_{\mathrm{abcd}} + R_{\mathrm{bcda}})}{2 \ln 2} f\left(\frac{R_{\mathrm{abcd}}}{R_{\mathrm{bcda}}}\right)$$

where d is the thickness of the crystal and the function f is

$$f \simeq 1 - \left\{\frac{R_{\mathrm{abcd}} - R_{\mathrm{bcda}}}{R_{\mathrm{abcd}} + R_{\mathrm{bcda}}}\right\}^2 \ln 2$$

$$- \left\{\frac{R_{\mathrm{abcd}} - R_{\mathrm{bcda}}}{R_{\mathrm{abcd}} + R_{\mathrm{bcda}}}\right\}^4 \left\{\frac{(\ln 2)^2}{4} - \frac{(\ln 2)^3}{12}\right\}.$$

By R_{abcd}, etc, we mean the potential drop across AB for unit current between C and D.

The measurements were made using an electrometer triode bridge to detect the out-of-balance voltage between the source and a potentiometer. A switch was arranged to apply a stabilised current to any pair of contacts, and to measure the voltage across a pair of contacts or across a standard resistance.

The crystal was mounted on a silica slide and could be held at temperatures between 17 and 200° C.

The resistivity of reduced crystals was measured and the results are shown in fig. 2. The Hall voltage was too small to measure relative to noise in all cases. There were rather large fluctuations, such that the Hall voltage could not be measured for a Hall mobility below 0.1 cm^2 V^{-1} sec^{-1}. The resistance decreased at first, followed by a rise as reduction proceeded, in agreement with the two-probe measurements previously reported [12] on crystals grown in this laboratory.

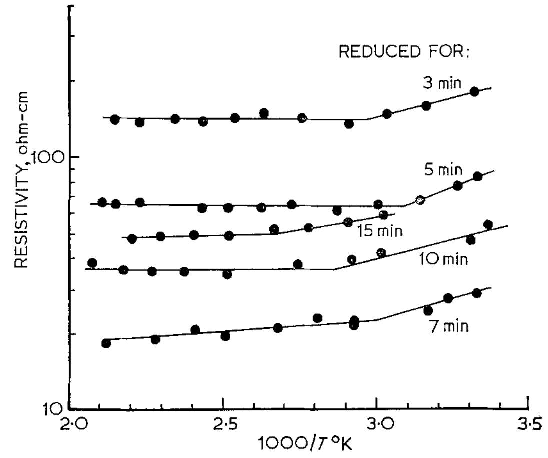

Figure 2 Resistivity of reduced crystals.

4. Seebeck Coefficients

The Seebeck coefficient α was measured by setting up temperature differences up to 2° between the ends of the specimen, measured with fine copper-constantan thermocouples. The voltages (between the copper components) were measured using a microvoltmeter. The results on reduced crystals are shown in fig. 3. For 7 and 15 min reduction times there is little, if any, variation of α with T. The material is n-type.

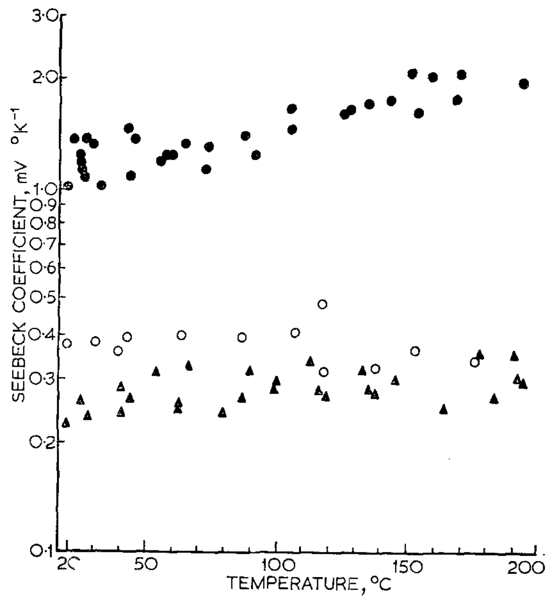

Figure 3 Seebeck coefficient of reduced crystals. Reduction times: ●, 3 min; ▲, 7 min; ○, 15 min.

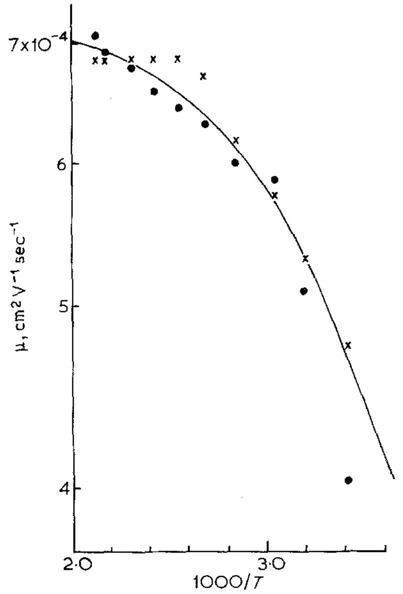

Figure 4 Small polaron mobility. ●, 7 min; ×, 15 min.

5. Interpretation via Polarons

In [12] the values of ρ and α were interpreted supposing a conventional band model, with optical mode scattering and an effective electron mass of 4.5 m_0. This led to carrier concentrations from 1 to 7.5×10^{19} cm^{-3} and a room temperature mobility of 3×10^{-3} cm^2 V^{-1} sec^{-1}. This is too small, however, to be consistent with a wide band model, and indicates that small polarons are involved, which is to be expected in a highly ionic lattice. This conclusion is supported by the fact that the mobility calculated by the above procedure rises with temperature between 0 and 200° C.

The results have therefore been re-interpreted assuming a small polaron hopping model. The expression for α now has the simple form $\alpha = k/e \ln N_c/N$ [9], where N is the concentration of polarons and N_c that of the positive ion sites at which electrons can be trapped. In $BaTiO_3$, this is the concentration of Ti^+ ions, which is 1.56×10^{22} cm^{-3} in stoichiometric material. After 7 and 15 min reduction, the values of α are 300 μV ° C^{-1} and 380 μV ° C^{-1} respectively at 20° C, and vary little with temperature. Thus N is independent of T with values of 4.2 and 1.9×10^{20} cm^{-3}.

These values of N, combined with the measured resistivity, lead to values of mobility rising to 7×10^{-4} cm^2 V^{-1} sec^{-1} at 500° K, fig. 4, and such that there is a linear relation between $\ln (\mu T^{3/2})$ and $1/T$ as shown in fig. 5. This is consistent with the mechanism of small polaron hopping, since the theory for this predicts [7, 9]

$$\mu \propto T^{-3/2} \exp(-W/kT).$$

The activation energy W has the value 0.074 eV.

The mobilities were the same for the 7 and 15 min reduction. If we suppose they are the same in all samples, the polaron concentrations for the different reduction times would be:

3 min in H_2 at 800° C 6.9×10^{19} polarons cm^{-3}
5 min in H_2 at 800° C 1.5×10^{20} polarons cm^{-3}
7 min in H_2 at 800° C 4.2×10^{20} polarons cm^{-3}
10 min in H_2 at 800° C 2.4×10^{20} polarons cm^{-3}
15 min in H_2 at 800° C 1.9×10^{20} polarons cm^{-3}

It is important here to note that in a material containing polarons, an absorption peak is expected to be present in the near infra-red at an energy $\mathbf{h}\nu = 4W$ [2, 4]. This leads to a wavelength $c\mathbf{h}/4W$, which is 4.2 μ for $W = 0.074$ eV. The reflectance of reduced barium titanate single crystals has been studied by Reik and Heese [10], who found a peak at $\sim$ 4 μ in the real part of the conductivity.

6. Curie Point Variation

It was found that the Curie point was modified by the reduction process. Measurements were made by observing the domain walls in the crystals with a polarising microscope while vary-

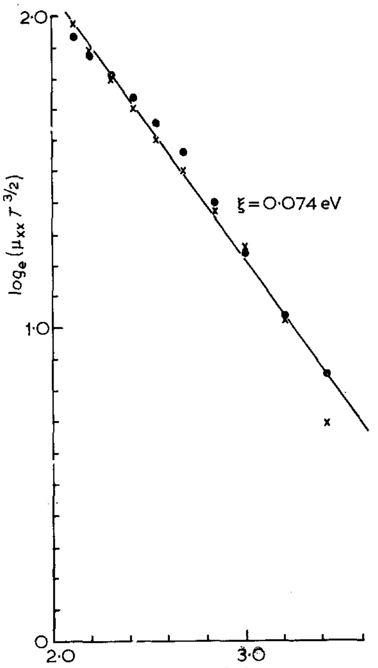

Figure 5 Plot of $\log_e (\mu_{xx} T^{3/2})$ against reciprocal temperature demonstrating small polaron hopping transport. ×, 7 min heat-treatment; ●, 15 min heat-treatment.

ing the temperature. Below the Curie point the *c*-axis of the different domains lies in the plane of the crystal parallel to one or the other of its shorter sides. Above the Curie point the crystals are no longer birefringent, leading to a sensitive method of determining the Curie point which is not affected by changes in conductivity. Attempts to measure dielectric constant and to observe hysteresis loops were made, but were only satisfactory while the resistivity remained high. The variation in Curie point with time of reduction is shown in fig. 6.

It appears that these results can be explained using the theory of Jaynes [8]. This accounts for the ferroelectric properties of $BaTiO_3$ in terms of the polarisability of the oxygen valence electrons as well as the contribution due to the ions and lattice displacements. The expression obtained by Jaynes for the Curie point T_c is

$$2K/(1 + K) = \tanh \epsilon/kT_c$$

where 2ϵ is the energy of the first excited state of the electronic structure of the oxygen octahedron,

$$K = \frac{\epsilon v(1 - \beta \nu)}{\mu^2 \beta}$$

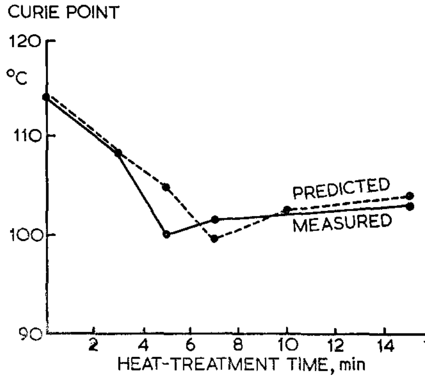

Figure 6 Comparison of predicted and measured Curie temperatures.

where v is the volume of the unit cell, β is the Lorenz factor, ν is the combined polarisability due to ions and lattice displacements and μ is the dipole moment arising from the electron states. The electrons considered by Jaynes are those forming the valence (oxygen 2p) band. The creation of n free polarons implies the existence of n donor centres. Assuming that these are oxygen vacancies, the population of 2p electrons would be reduced by the factor $(1 - n/N)$, which will correspondingly reduce the value of K and therefore of T_c.

The density N of valence electrons in the octahedral structure of a stoichiometric crystal is 4.5×10^{22} cm^{-3}, and the maximum polaron density obtained in reduction was 4.2×10^{20} cm^{-3}. This represents a depletion of the 2p levels by 0.9%, which would correspond with a reduction in T_c of 14°, as observed. Using the polaron concentrations estimated as above assuming the same mobility in all crystals, the calculated Curie point is compared with the observed in fig. 8. This agreement supports the estimates of the polaron density.

7. Discussion

It is appreciated that our estimated drift mobility is considerably less than the average value of Hall mobility measured by Berglund and Baer [3]. However, with hopping polaron transport the ratio of Hall to drift mobility may be large (Holstein and Friedman [6]). They give for the ratio

$$\mu_H/\mu_D = \frac{kT}{J} \exp \frac{2}{3} \frac{W}{kT}.$$

To estimate J, half the band width for a rigid lattice, we use Holstein's 1959 expressions for non-adiabatic small polarons:

$$\text{drift mobility} = \mu_D = \frac{ea^2}{kT}p$$

where p is the hopping probability,

$$p = \frac{1}{\mathbf{h}}\left(\frac{\pi}{WkT}\right)^{1/2} J^2 \, e^{-W/kT}$$

where W is the polaron hopping energy $=$ 0.074 eV. We find p at 20° C $= 7.4 \times 10^9$ sec^{-1} and $J = 0.005$ eV.

Thus μ_H/μ_D becomes 80 at 300° K, and μ_H could be about 4×10^{-2} cm^2 V^{-1} sec^{-1}. This is below our limit of measurement, as indicated in section 2. It is also less than the value of μ_H observed by Berglund and Baer in the c-direction, i.e. 0.13 cm^2 V^{-1} sec^{-1}. In the present work the current flow is in the plane containing the c-axis, on average at 45° to the axis. Our lower value is unlikely to be associated with crystal symmetry, and may be the result of impurities.

With such a small value of J, it is possible that the hopping process is between impurity atoms and is not characteristic of the crystal lattice. However, the Curie point results give indirect evidence that the mobility is the same for all samples, independent of reduction time. Thus the oxygen vacancies are not likely to be the relevant impurities.

It may be noted that if the hopping is between Ti^+ ions, $a = 5 \times 10^{-8}$ cm, the polaron radius $r_p = \frac{1}{2}(\pi/6)^{1/3}$, a [2] has the value 2×10^{-8} cm and the rigid band mass $= \mathbf{h}^2/2Ja^2$ is about 100 m_0.

Acknowledgement

DLR wishes to express his gratitude to the CEGB for financial support during the period when the work was undertaken.

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Received 11 February and accepted 24 March 1970.