

LOWERING THE CURIE TEMPERATURE IN REDUCED BaTiO₃

K.H. Härdtl and R. Wernicke

Philips Forschungslaboratorium Aachen GmbH, Aachen

(Received 30 October 1971 by G.W. Rathenau)

N-type conductivities between 1 and 10 (Ωcm)⁻¹ were obtained in polycrystalline BaTiO₃ samples by reduction. Assuming the mobility $\mu = 0.5 \text{ cm}^2/\text{Vsec}$, the electron densities of these reduced BaTiO₃ samples were calculated from the measured conductivities. The Curie temperatures were determined by dilatometric measurements. The experiments reveal a linear decrease in the Curie temperature of 50°C per 10²⁰ electron/cm³ for electron densities below 10²⁰ cm⁻³ and of 41°C per 10²⁰ electrons/cm³ for electron densities above 10²⁰ cm⁻³. The results are compared with various models found in the literature.

1. INTRODUCTION

GENERALLY in ferroelectric materials even slight perturbations within the lattice result in a shift of the Curie temperature. Changes in the Curie temperature can therefore also be expected to occur when these materials are changed by suitable means to a semiconducting state. This change can be achieved by appropriate doping or by reduction, i.e. by the formation of oxygen vacancies.

While a shift in the Curie temperature due to the addition of different doping elements has been reported by various authors,¹ Chebkasov² was unable to observe any change in the Curie temperature of reduced BaTiO₃. On the other hand, Bursian³ found that the Curie temperature of reduced BaTiO₃ crystals decreased with increasing conductivity.

We will now consider the effect of the degree of reduction on the Curie temperature of BaTiO₃ samples. The observed linear decrease in the Curie temperature with the electron density will be compared with various theoretical considerations found in the literature.

2. PREPARATION OF THE SAMPLES

Due to the lack of suitable crystals the investigations were performed on ceramic BaTiO₃ samples prepared by the conventional sintering method. The starting materials, BaCO₃ and TiO₂, were stoichiometrically proportioned, ball-milled and presintered at 1050°C. The calcined powders were thoroughly ground and after hydrostatic pressing, the samples were sintered for several hours at 1350°C in an oxygen atmosphere. The resulting samples were single-phased with a density of approximately 97% of the theoretical value. Small plates were sawn from these sintered samples and polished to a size of 15 × 5 × 0.6mm. These were reduced at temperatures between 800 and 1150°C in a quartz tube with a flowing (75%N₂–25%H₂) atmosphere. Rapid cooling of the samples after about 60 min reduction ensured that the high temperature reduction conditions was 'frozen in'.⁴

3. MEASUREMENTS AND RESULTS

Using the reduction method described above, samples with *n*-type conductivities between 1 and 10 (Ωcm)⁻¹ could be prepared. It is a well-known fact,⁵ however, that grain boundary resistances can occur in semiconducting BaTiO₃ ceramics,

which are so high in comparison with the resistances of the grains that they determine the total resistance of the sample. In this case a calculation of the electron density in the grains is impossible. Therefore it is of great importance to check whether grain boundary resistances are present or not. The relation between thermoelectric powder η and electrical conductivity σ is investigated for this purpose. If grain boundary resistances are absent, a straight line with the slope $-k/e$ is found for the relation $\eta = f(\ln\sigma)$.⁴ As Fig. 1 shows, this dependence is closely satisfied for the samples, so that the measured electrical conductivity is determined only by the grain properties. In this case the concentration n of the conduction electrons is easily found by using the known value for the mobility of free carriers $\mu = 0.5 \text{ cm}^2/\text{Vsec}$.^{4,6}

Since the determination of the Curie temperature by the conventional measurement of the dielectric constant is not possible because of the high electrical conductivity, it was found dilatometrically by plotting the thermal expansion versus the temperature of the samples on a X - Y recorder. The transition from the tetragonal phase to the cubic one is accompanied by a change in volume of the unit cell, which consequently results in a characteristic shrinkage of the sample.⁷ This is shown in Fig. 2 for an unreduced and therefore nonconductive sample, which allows the conventional dielectric determination of the Curie temperature. As shown in Fig. 2, the Curie temperatures obtained from both methods are in good agreement. It was observed that the shrinkage was spread out over a wider temperature range as the conductivity increased.

The measurements were carried out with a set of six samples, which were reduced at different temperatures rising from experiment to experiment. After each reduction the conductivity, thermoelectric power and Curie temperature were determined and analyzed in the manner outlined above. Figure 3, in which the shift of the Curie temperature ΔT is plotted versus the free-carrier concentration shows, in the lower range, a linear increase which continues into the upper range with a slightly changed slope. Since the backward extension of this straight line passes through the origin, it is thought that one of the physical

parameters which determines the slope of the straight line $\Delta T_c = f(n)$ changes by a certain amount in the neighbourhood of the saddle point.

4. DISCUSSION OF RESULTS

The lattice defects caused by the reduction of BaTiO₃ are primarily concerned with the formation of oxygen vacancies and consequently with the generation of free carriers. An attempt will now be made to describe the effect of free carriers on the Curie temperature with the aid of two different models based on the work of Fridkin⁸ and Hallers,⁹ respectively.

On the basis of Devonshire's thermodynamic considerations Fridkin⁸ extends the usual expansion of free energy by an additional term $n \cdot E_g$ which refers to the additional energy of the electronic subsystem. The shift of the energy-band edge ΔE_g occurring at the Curie temperature is described as a consequence of the polarisation P_0 and leads, after appropriate calculation, to the following expression for the lowering of the Curie temperature ΔT_c

$$\Delta T_c = T_c^0 - T_c^1 = 2\epsilon_0 \frac{C \Delta E_g \cdot n}{P_0^2}$$

C = Curie constant

ΔE_g = shift of energy-band edge at Curie temperature

P_0 = spontaneous polarisation at Curie temperature

T_c^0 = Curie temperature in the unreduced state

T_c^1 = Curie temperature in the reduced state

Using the values applicable to BaTiO₃ ($C = 2 \cdot 10^5 \text{ }^\circ\text{K}$,¹⁰ $\Delta E_g = 2 \cdot 10^{-2} \text{ eV}$,¹¹ $P_0 = 18 \text{ } \mu\text{C}/\text{cm}^2$ ¹⁰), we obtain a shift of the Curie temperature shown in Fig. 3 by the dot-and-dash line, which gives satisfactory agreement with the measured values. The saddle occurring in the measured curve might be interpreted in this context as a change in physical parameters (e.g. ΔE_g , C). Hallers⁹ bases his consideration on a change in the ion-ion interaction resulting from screening by the free conduction electrons. From the condition that the frequency of the transverse optical mode in the long-wavelength

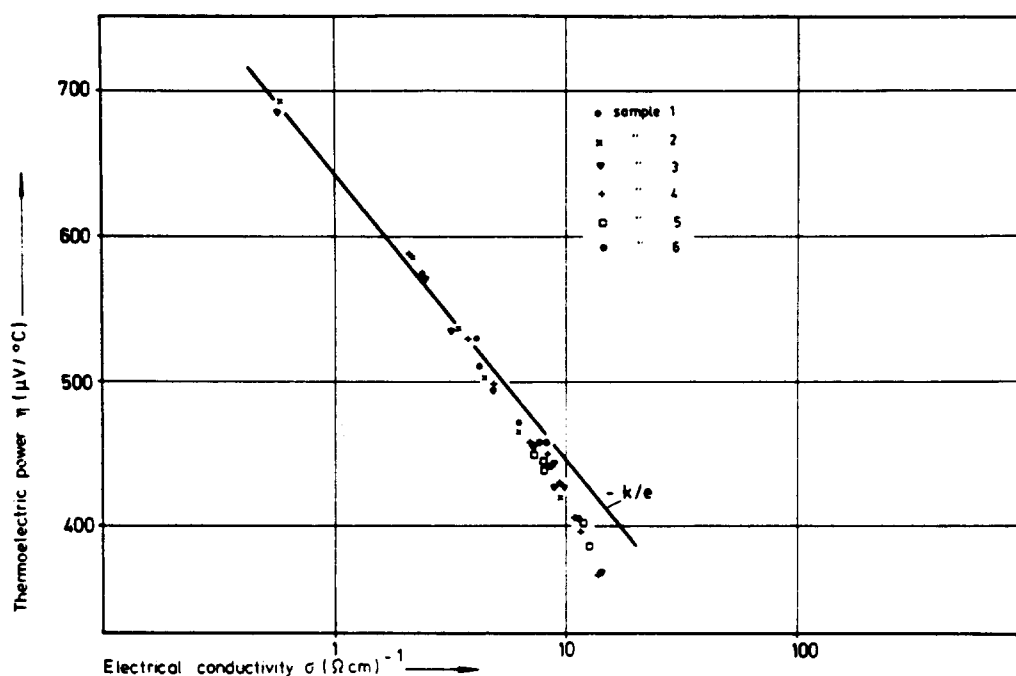


FIG. 1. Thermoelectric power η and conductivity σ of BaTiO₃ samples reduced at different temperatures.

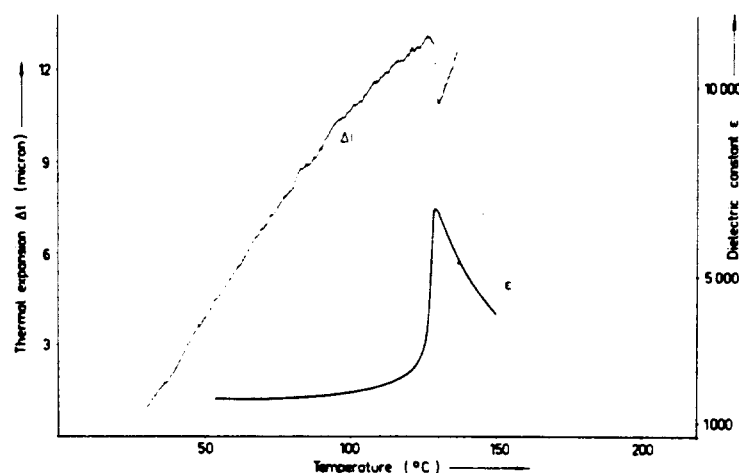


FIG. 2. Thermal expansion Δl and dielectric constant ϵ versus temperature.

limit tends towards zero, he finds a lowering of the Curie temperature of the form

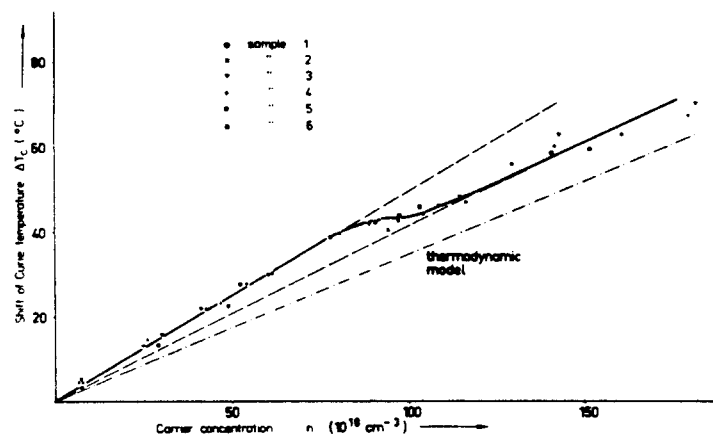
$$\Delta T_C = T_C^0 - T_C^1 = \frac{C}{1} [1 - G(\lambda a)]$$

C = Curie constant

$$\lambda^2 = \frac{e^2 \cdot n}{\epsilon_0 \epsilon_r k T} \text{ screening factor}$$

$2a$ = lattice constant

The function $G(x)$ here represents a characteristic lattice parameter, which was tabulated for the NaCl lattice by Hallers. For small screening factors this function differs little from unity. Thus, if we assume $\lambda a \ll 1$ this function can be applied to the perovskite lattice as a first approximation. Furthermore, the function $G(\lambda \cdot a)$ can in this case be approximated by a parabola:

Shift of Curie temperature ΔT_c versus carrier concentration n

$$G(\lambda a) \approx 1 - \alpha \lambda^2 a^2 \quad \text{with} \quad \alpha = 9 \cdot 10^{-2} \lambda a \ll 1.$$

For the lowering of the Curie temperature we thus obtain

$$\Delta T_c = T_c^0 - T_c^1 = \frac{C}{3} \alpha a^2 \frac{e^2 \cdot n}{\epsilon_0 \epsilon_r k T_c^1}$$

Here again, we find a linear dependence as a first approximation ($T_c^0 \gg \Delta T_c$) but this can only be brought into agreement with the measured results if values between 100 and 200 are assumed for the dielectric constant at the Curie temperature where values of about 8000 are normally found. It was not possible to establish unambiguously whether the dielectric constant in fact has these values for the corresponding frequency of the transverse optical mode. Another objection to the application of the model to BaTiO₃ is the question whether or not the dielectric relaxation time $\tau = \epsilon_0 \epsilon_r / \sigma$ is too large for the optical modes.

A further possible explanation is that the lowering of the Curie temperature is attributable

to the effect of oxygen vacancies formed at the same time as free electrons in the reduction process. It is known from other investigations¹ that changes in the cationic lattice (e.g. due to vacancies, impurity ions) lead to a shift in the Curie temperature, even in the absence of free carriers. It is therefore conceivable that similar effects occur with changes in the anionic lattice (e.g. oxygen vacancies). As earlier thermogravimetric investigations have shown,¹² all oxygen vacancies can be assumed to be singly ionised at room temperature. In this case the concentration of oxygen vacancies is equal to the concentration of free conduction electrons. There is then, in accordance with Fig. 3, a lowering of the Curie temperature by 41 and 50°C, respectively, per 10^{20} oxygen vacancies/cm.³ Since experimental separation of the effects of oxygen vacancies and free carriers in BaTiO₃ is extremely difficult, it is impossible at present to make any definite statement about the mechanism to which the lowering of the Curie temperature is in fact attributable.

REFERENCES

1. MARTIN, H.J., *Die Ferroelektrika*, Geest u. Portig, Leipzig (1964).
2. CHEBKASOV, A.V., *Izv. Akad. Nauk SSSR, Ser. Fiz.* **29**, 1001 (1965).
3. BURSIA, E.V., *Sov. Phys. -Solid State* **11**, 2423 (1970).
4. GERTHSEN, P. *et al.*, *Phys. Status Solidi* **11**, 303 (1965).

5. HAAYMAN, P.W., *et al.*, *DBP* **929**, 350 (1955).
JONKER, G.H., *Solid-St. Electron.* **7**, 895 (1964).
HEYWANG, W., *Solid-St. Electron.* **3**, 51 (1961).
6. BERGLUND, C., *Phys. Rev.* **157**, 358 (1967).
7. SHIRANE, G. *et al.*, *J. Phys. Soc., Japan* **7**, 1 (1952).
8. FRIDKIN, V.M., *ZhETF Pis. Red.* **3**, 252 (1966);
[*JETP Lett.* **3**, 161 (1966)].
9. HALLERS, J.J. *et al.*, *Phys. Status Solidi* **36**, 587 (1969).
10. JONA, F. and SHIRANE, G., *Ferroelectric crystals*. Pergamon Press (1962).
11. FRIDKIN, V.M. *et al.*, *Sov. Phys. – Solid State* **8**, 1287 (1966).
12. GERTHSEN, P. and HÄRDTL, K.H., unpublished.

In polykristalliner BaTiO₃ Keramik wurden durch Reduktion Elektronenleitfähigkeiten zwischen 1 und 10 (Ωcm)⁻¹ erreicht. Aus Messungen der Leitfähigkeit konnte unter Vorgabe der Beweglichkeit ($\mu = 0,5 \text{ cm}^2/\text{Vsec}$) die Elektronendichte berechnet werden. Die Curiepunktbestimmung erfolgte dilatometrisch. Die Experimente ergeben eine lineare Abnahme der Curietemperatur von 50°C pro 10²⁰ Elektronen/cm³ für Trägerdichten unterhalb von 10²⁰ cm⁻³ und von 41°C pro 10²⁰ Elektronen/cm³ für Trägerdichten oberhalb von 10²⁰ cm⁻³. Die Ergebnisse werden mit verschiedenen Modellen aus der Literatur verglichen.