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Semiconducting Barium Titanate

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Barium titanate, which is well known as a basic ferroelectric material, is also of interest when doped because of the interaction between semiconductivity and ferroelectricity. The resistance of blocking layers at surfaces and grain-boundaries is governed mainly by the ferroelectric properties, so that a resistance jump of four decades is observed on heating above the Curie temperature. A survey of the chemical and physical properties of such blocking layers both at surfaces and interfaces is presented.

Doped titanates have been used as the basis of two new types of material:
(1) Semiconductors with high positive temperature-coefficient of resistivity in special temperature ranges suitable for temperature-sensors and stabilisers.
(2) Dielectrics with extremely high dielectric constant, used in so-called barrier-layer condensers.

1. Introduction

The technical value of semiconducting $BaTiO_3$ is based on the interaction of conductivity on the one hand and the special ferroelectric properties of this material on the other. Thus, before speaking about this interaction it is convenient to recapitulate briefly the basic features of the ferroelectric behaviour of $BaTiO_3$ and also the doping properties of this high-band-gap semiconductor which is normally an insulator.

2. Ferroelectricity

Above the Curie temperature ($T_c = 110°C$) the dielectric constant ϵ of $BaTiO_3$ (fig. 1a) follows a Curie-Weiß law

$$\epsilon = \frac{C}{T - T_c} \qquad (1)$$

with a rather high Curie constant $C = 1.7 \times 10^5$ K. Just before ϵ reaches ∞ at 120°C a spontaneous polarisation develops, and this causes a small lattice distortion of about 1 %, so that the original cubic symmetry of the perovskite lattice is lost, leading to a tetragonal symmetry (fig. 1b) Owing to this fact ϵ becomes anisotropic as shown in fig. 1a. With decreasing temperature the dielectric constant $\epsilon_\perp$ perpendicular to the spontaneous polarisation increases again; the remaining two former cubic directions also develop a spontaneous polarisation, first at about 5°C and again at −70°C, leading to an orthorhombic and a rhombohedral lattice symmetry respectively.

Just as in a ferromagnetic material, domains are formed with uniform homogeneous polarisation, the orientation of which changes from domain to domain and is randomly distributed, especially in polycrystalline ceramic materials.

These materials have become of high technical interest owing to the high dielectric constant. But since the domain orientation is not fixed, the dielectric behaviour becomes rather complicated. This will not be discussed here in detail. Only one feature is mentioned at this point: in the ferroelectric temperature range one has to distinguish between small and large-signal dielectric constants (cf. $\bar{\epsilon}$ and ϵ_{eff} respectively in fig. 5). Whereas the former describes mainly the field-induced polarisation, the latter is mainly determined by switching of the spontaneous polarisation.

3. Bulk Conductivity

Owing to its band gap of about 3 eV [1], undoped $BaTiO_3$ ceramic is – as already mentioned – an insulating material with a resistivity of more than $10^{10}\,\Omega$ cm at room-temperature. An n-type conductivity can easily be achieved by partially reducing Ti^{4+} according to the equation

$$Ti^{4+} + e^- \rightarrow Ti^{3+}$$

The additional electrons (e^-) are not localised at room-temperature.

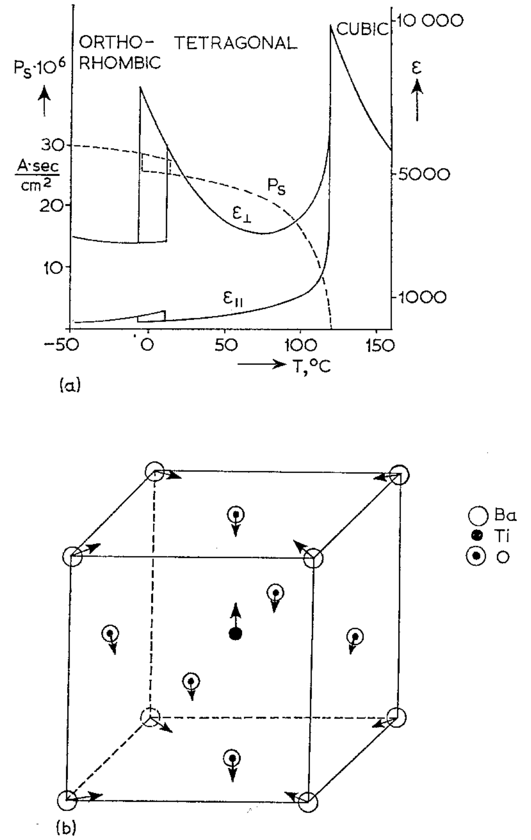

Figure 1 (a) Dielectric behaviour and spontaneous polarisation of $BaTiO_3$.(b) Perovskite lattice. The arrows indicate the ion displacements at the transition from the cubic to the tetragonal phase.

As an explanation for the resulting conductivity Saburi [2] has proposed a hopping model whereas Gerthsen *et al* [3, 4] have presented a polaron theory, both papers referring to measurements obtained with polycrystalline materials. Reduced single crystals were studied by Ikushima and Hayakawa [5]; their results agree well with a polaron model, the effective mass of the polaron being estimated to be equal to about twenty free electron masses m_0.

A detailed investigation of mobility and band structure of $BaTiO_3$ single crystals was carried out independently by Berglund and Baer [6] some results from which are shown in fig. 2. The mobility has been found to be about 0.5 cm²/Vsec. above the Curie temperature, corresponding to an effective mass of 6.5 m_0. Below the Curie temperature the mobilities diverge because of the lattice distortion. No resistivity jump similar to that found by Ikegami and Ueda [7] at all transition points occurred at the Curie point.

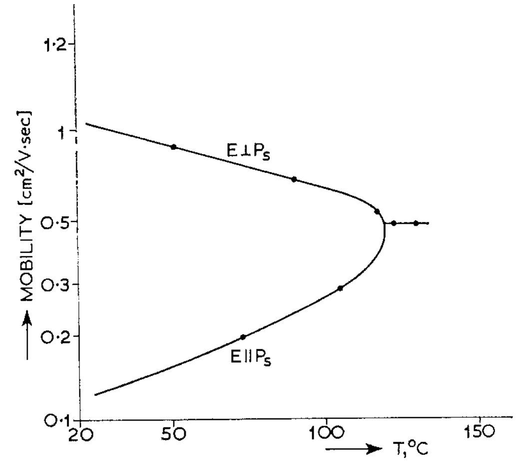

Figure 2 Mobility anisotropy in $BaTiO_3$ (after Berglund and Baer [6]).

From the given values of the effective masses one estimates a width of the conduction band of the order of 0.1 eV. Thus the density of states is nearly equal to the density of lattice cells in the normally interesting temperature range.

The above-mentioned reduction of Ti^{4+} can be achieved either by annealing in a reducing atmosphere, leading to oxygen vacancies, or by partially substituting Ba^{2+} or Ti^{4+} by ions of higher valency. An analogous substitution of Ba^{2+} or Ti^{4+} by ions of smaller valency does *not* lead the material to *p*-type conductivity at room-temperature. Since higher valency states than two for Ba or four for Ti are not possible, the overall neutrality is achieved by formation of oxygen vacancies. Ikushima and Hayakawa [8] have even found $BaTiO_3$ containing a small amount of Ag^+ incorporated on Ba^{2+} sites to be *n*-type conductive. This effect has been explained by the assumption of formation of oxygen vacancies with electron capture. *P*-type conductivity was found in polycrystalline $BaTiO_3$ only at elevated temperatures, owing to deep traps [9]. But since these traps were mainly incorporated at interface boundaries the possibility cannot be excluded that this is mainly an interface conductivity.

In spite of the existence, under most circumstances, of only one single conduction type in $BaTiO_3$, blocking layers are decisive for many scientifically and technically interesting effects in semiconducting $BaTiO_3$. In what follows we try to present a systematic survey of these effects without taking into account the history of their detection and explanation.

As already mentioned, oxygen vacancies as well as special metal ions can act as donors, the activation energy of which is in the order of 0.1 eV [10]. Owing to this high value of activation energy, as compared with Ge or Si, the donors are totally ionised only at temperatures higher than – 30° C. Below this temperature one finds a corresponding increase of bulk resistance (fig. 16).

Since the concentration of oxygen vacancies cannot be easily controlled, they are only used when very high doping is desired.

For concentrations less than 10^{19} cm^{-3} a well defined doping is reached by the above-mentioned controlled valency substitution method, leading to a lattice free from vacancies, e.g. in the case of La corresponding to a composition

$$(Ba_{1-x}La_x)(Ti_{1-x}{}^{4+}\,Ti_x{}^{3+})\,O_3\,.$$

This has been proved experimentally for $x < 0.1\,\%$. The conductivity increases with dopant concentration up to this limit. Surprisingly, for higher concentrations, the conductivity once more declines [11-13], as may be seen in fig. 3 for different kinds of dopants, all of which show the same effect. This cannot be explained by a solubility limit of donors. The decay of conductivity at higher concentrations can only be understood in terms of the influence of acceptor traps compensating for these donors. There is strong evidence that this is connected with a pairing of the dopant ions. Two neighbouring Ba^{2+} ions are replaced by two La^{3+} ions [14], for example, and a barium vacancy is coupled to this pair, forming a double acceptor trap.

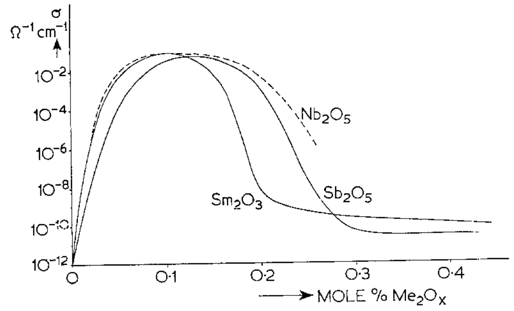

Figure 3. Conductivity versus doping concentration.

In the case of Sb-doping, which is of considerable technical interest, this effect was extensively investigated by Eberspächer [15] and Schmelz [16], who mainly used X-rays for determining the lattice constants and neutron diffraction for determining the lattice sites of the incorporated ions. When the starting mixture of the oxides corresponds to a net formula $Ba(Ti_{1-x}Sb_x)O_3$ no semiconductivity is found and both lattice constants and neutron diffraction indicate an incorporation of equal numbers of Sb^{3+} and Sb^{5+} ions on Ti sites. Estimating the mutual attraction of these ions one comes to the conclusion that Sb^{3+} and Sb^{5+} are paired. Such pairing may in addition explain the extremely high shift of the Curie point observed in these materials [17]. Starting mixtures corresponding to a net formula $(Ba_{1-x}Sb_x)TiO_3$, have led to single-phase materials only in a very narrow concentration range. Here semiconductivity is observed as expected from the chemical formula. At higher concentrations Sb is incorporated also on Ti sites thus avoiding creation of Ti^{3+} ions, as may be seen from the formula

$$(Ba_{1-u}{}^{2+}\,Sb_u{}^{3+})(Sb_{u+v}{}^{3+}Sb_v{}^{5+}Ti_{1-u-2v}{}^{4+})O_3.$$

The excess Ti is found in a glassy sintering phase between the grains of the ceramic. It is to be noted here that this "interphase" is of great importance for the observed behaviour of all polycrystalline semiconducting titanates.

4. Barrier Layers

Owing to the fact that only *n*-type conductivity exists in $BaTiO_3$, blocking layers cannot be formed in the bulk. Nevertheless, surface or interface blocking layers are decisive for many effects. Two types of barrier layers have been observed:

(i) Surface barriers existing at metal contacts and
(ii) Interface or heterojunction barriers.

4.1. Surface Barriers

The first interest in these barriers arose from the possibility of getting high-permittivity capacitive layers on reduced $BaTiO_3$ (so-called surface barrier condensers). These can be produced, for instance, by silver-plating on reduced $BaTiO_3$ samples. Their rectifying properties have been investigated by Murakami [18]. A general investigation of the blocking properties of various metal contacts on $BaTiO_3$ ceramics was carried out by Seiter [19], the result can be seen in fig. 4. Here the ratio of contact resistance to bulk resistance is plotted versus the enthalpy of the first oxidation step of these metals. In all cases where the metal is so noble that Ti^{4+} cannot be reduced, a high blocking resistance is

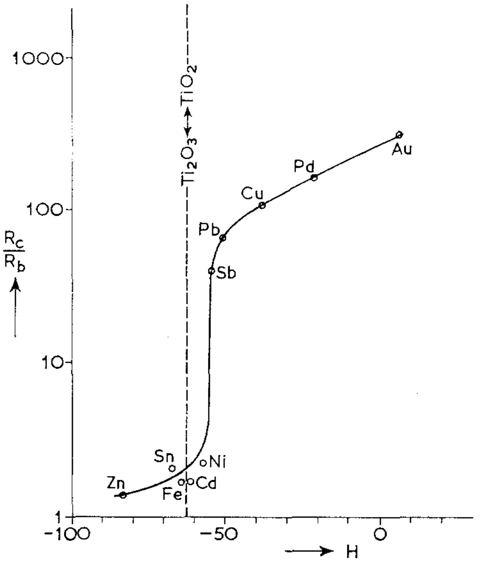

Figure 4 Contact resistance. The ratio of contact to bulk resistance R_c/R_b measured with samples for 1 mm thickness is plotted versus the reaction enthalpy, H, of the first oxidation step of the used contact metal.

observed, whereas metals reducing Ti^{4+} to Ti^{3+} produce ohmic contacts. The latter can probably be understood in terms of a surface layer with very high carrier concentration due to reduction by the metal contact. To what extent the blocking effect is also influenced by an oxygen excess [20] can be established only by further investigations.

For the technical application of surface barrier capacitors these pure Schottky barriers normally exhibit too small a breakdown voltage. Thus capacitors that are made by reducing $BaTiO_3$ ceramics to high conductivity and afterwards oxidising them to form a thin surface layer with good insulation between the conducting bulk and the blocking metal contact – normally silver – are to be preferred [21].

4.2. Interface Barriers

The main interest in $BaTiO_3$ is caused by the resistivity anomaly connected with interface blocking layers. As shown in fig. 5, the resistivity ρ of a doped ceramic $BaTiO_3$ sample increases sharply when it is heated above the Curie temperature. This increase can be explained in the following way [10, 22, 23]. Owing to acceptor states at the interface (fig. 6a) a space charge layer is formed at the surface of the $BaTiO_3$ grains, the thickness d, of which is determined by the relation

$$n_D \,.\, d = N_A^- \qquad (2)$$

where N_A^- denotes the number of occupied surface states and n_D the bulk donor concentra-

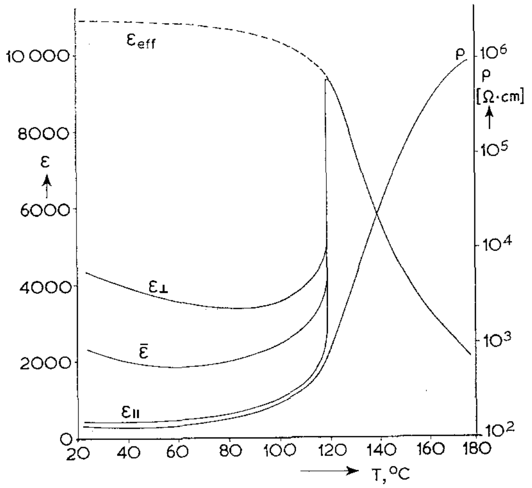

Figure 5 Dielectric constants of $BaTiO_3$ and resistivity of doped $BaTiO_3$ ceramics:
ρ: $BaTiO_3$ ceramic doped with 0.1% Sb_2O_3.
$\varepsilon_\perp$: single crystal, perpendicular to polarisation.
$\varepsilon_{\parallel}$: single crystal, parallel to polarisation.
$\bar{\varepsilon}$: ceramic, small a.c. field.
ε_{eff}: ceramic large a.c. field.

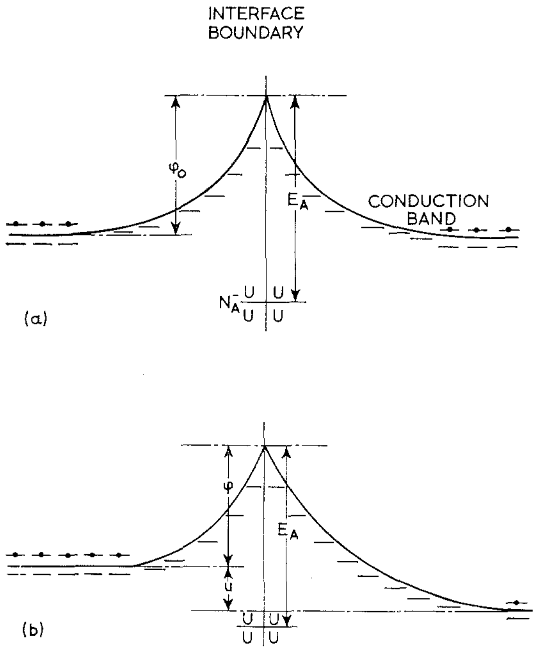

Figure 6 Band model of a barrier layer.

tion. According to Poisson's relation the barrier height ψ_0 is given by

$$\psi_0 = \frac{e^2 n_D}{2\epsilon\epsilon_0} d^2 \qquad (3)$$

Owing to these barriers the average resistivity is increased approximately by a factor exp (ψ_0/kT) as compared with the bulk resistivity and from the resistance increase above the Curie temperature one estimates [10] a value

$$\psi_0 \approx 0.55 \text{ eV}.$$

Below the Curie point this calculation has to be modified because a part of the negative charge stored in the surface states is compensated by the vertical component of the spontaneous polarisation [12]. According with this charge the positive head of the ferroelectric domains is directed toward the grain surface. The corresponding negative tail in the interior of the grain must be compensated by the positively charged donors [24]. From the value of the spontaneous polarisation and the donor concentration one may calculate that the penetration depth d_P of these domain tails must be of the order of 0.1 μm which is within the range of the depletion layer thickness. Thus one arrives at a model as shown in fig. 7. In this case where the domain tails are found in the space-charge region one may describe the contribution of the spontaneous polarisation to a first approximation by a high effective dielectric constant ϵ_{eff}, as was done in earlier publications [10, 22]. This effective dielectric constant can be measured directly when applying high a.c. signals of low frequency to insulating $BaTiO_3$, for in this case the contribution of orientation polarisation prevails throughout the bulk. One finds an almost constant value of ϵ_{eff}, of the order of 10^4 below the Curie point (fig. 5). Using this value, one calculates a barrier height $\psi_0 \approx 0.08$ eV at room temperature which agrees fairly well with the voltage-dependence of resistance found at 20°C (fig. 8). It should be emphasised, however, that ϵ_{eff} may offer only a first, rough indication of the effects below and near T_C, the more so as it is not yet known whether all surface domains really end in the space charge region.

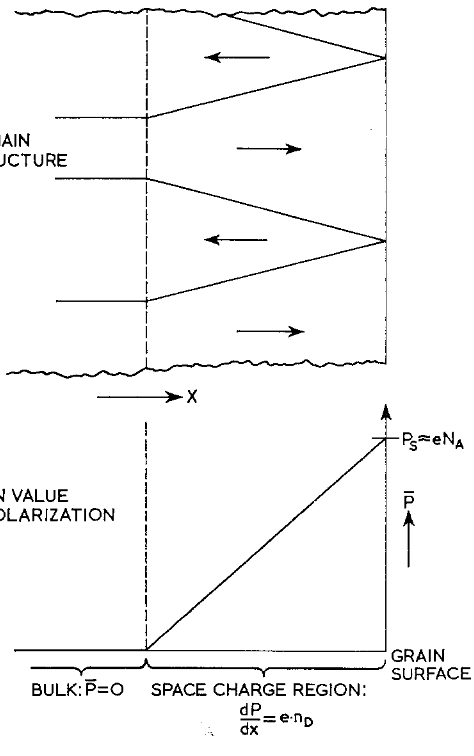

Figure 7 Domain-configuration at grain-boundaries and decay of polarisation in the grain-interior.

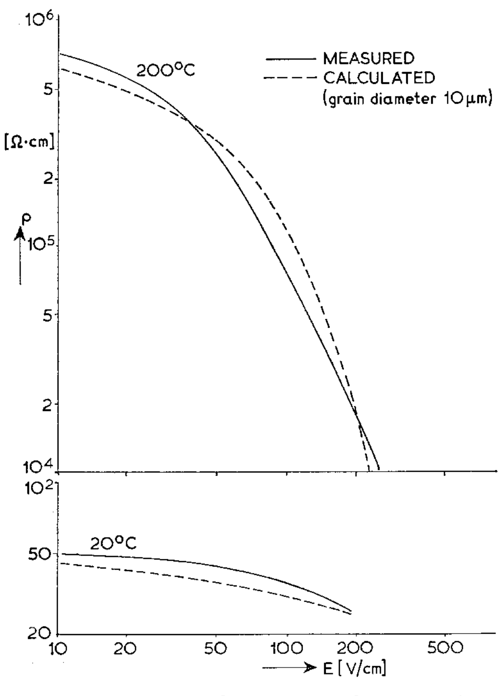

Figure 8 Dependence of resistivity of semiconducting $BaTiO_3$ ceramics on external field strength.

On heating above the Curie point the spontaneous polarisation disappears and the jumps

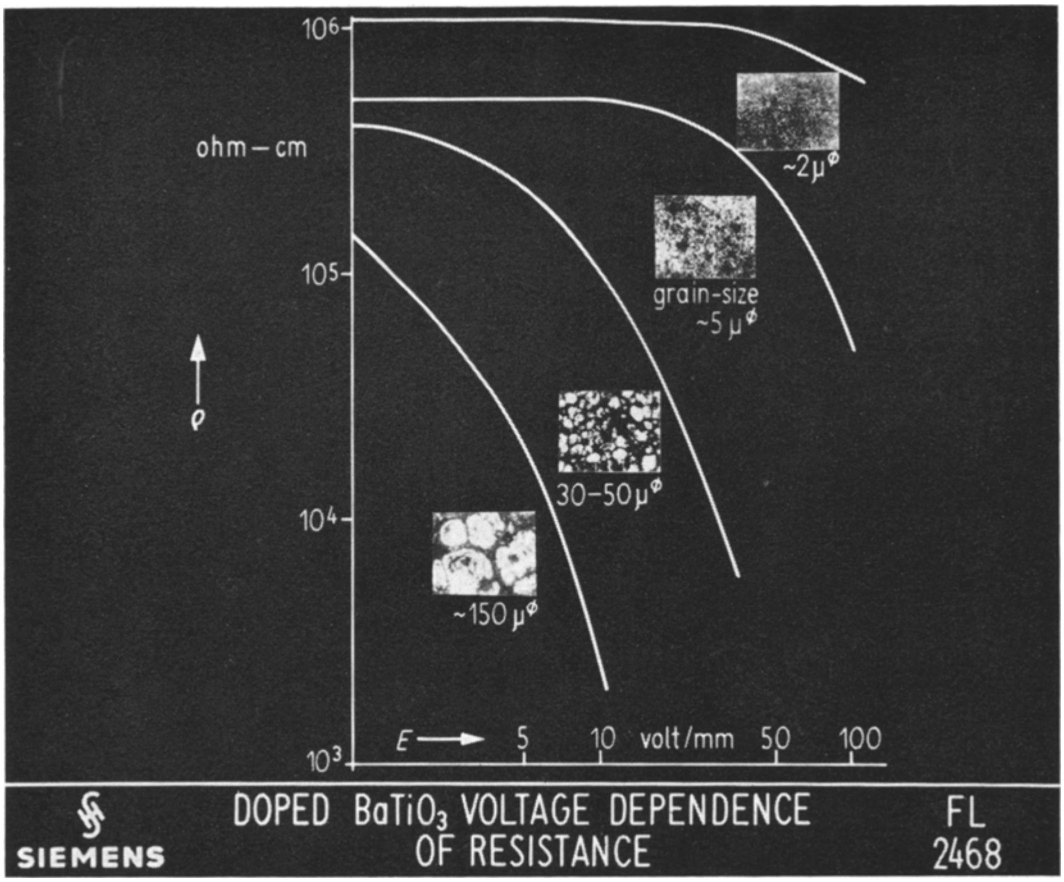

Figure 9 Voltage dependence of resistance of doped $BaTiO_3$.

which are sometimes observed in the temperature /resistance curve [12] can probably be explained by this. Normally these jumps are small because of the high value of ϵ_{eff} in the neighbourhood of T_c. When the temperature is further raised, ϵ decays according to the Curie-Weiß law. Thus ψ_0 must increase until the interface states have reached the Fermi level ζ, then N_A^- decreases owing to re-emission of electrons into the bulk. Thus ψ_0 asymptotically approaches the value $E_A - \zeta$, where E_A is the activation energy of surface states. This behaviour corresponds to the observed resistivity curve with a maximum when the Fermi level is reached by the acceptor states. From the maximum of four decades of resistance increase reached in normal ptc-resistors* one calculates an activation energy of these surface states of the order of 0.9 eV [10].

Using Sb as a dopant, extremely high factors of increase of resistance, of the order of 10^9, can be achieved by special preparation methods [25]. This corresponds to an activation energy E_A of about 2 eV. In this special case, Sb is found enriched near the grain-boundaries, thus forming an insulating layer of $Ba(Ti_{1-x}Sb_x)O_3$ between the conductive interiors of the grains. The Curie point of this layer is found near room-temperature.

The barrier-layer model further explains the observed decay of resistivity with increasing average field strength E (fig. 8), for the barrier height ψ must decrease with increasing voltage u applied to a single barrier (fig. 6b). The smaller the grain size, the smaller is this *local* voltage u with a given external field strength E. Thus in fine-grain material the resistivity decay is observed only at higher values of E (fig. 9) than in coarse-grain material.

The most interesting problem connected with this model is the question as to the nature of the

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*ptc = positive temperature coefficient of resistivity.

interface states. Here the following investigations have given important further information:

(*a*) By a decoration method [26] and especially by ion-induced electron-emission microscopy [27, 28], the electric fields connected with the barrier layers can be made visible. They are seen as dark shadows at the grain boundaries perpendicular to the direction of the applied field in fig. 10. But these shadows do not exhibit the same width at all these grain boundaries. Mostly one finds them especially pronounced at those grain-boundaries which have a thick non-perovskite interphase.

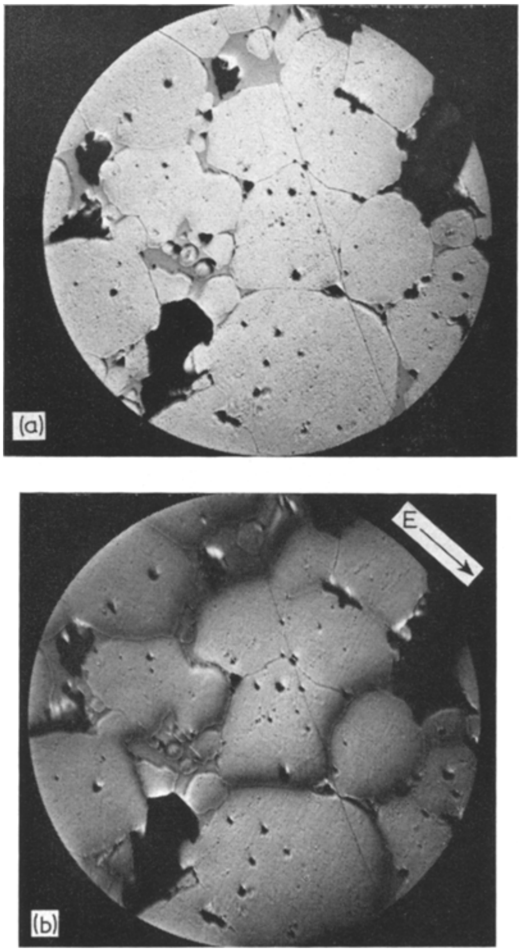

Figure 10 Semiconducting $BaTiO_3$ ceramic. Electron-emission microscopic image (a) without d.c. field (b) with a d.c. field applied in the direction of the arrow. The dark holes are due to grains broken out during grinding.

(*b*) The purer the raw material used, the smaller is the resistance anomaly (fig. 11, curve a). By adding copper or iron in concentrations from which ones calculates N_A according to the developed model, an optimum resistance increase can be achieved (fig. 11, curve b) [9].

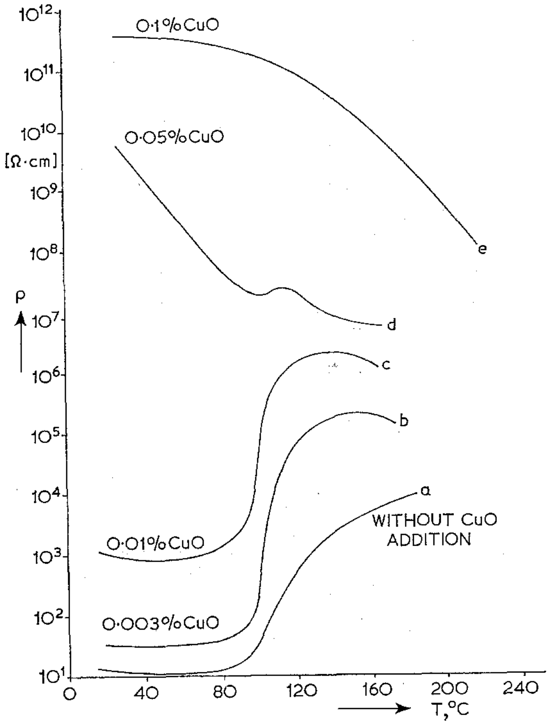

Figure 11 Resistivity versus temperature characteristics of Sb-doped high purity $BaTiO_3$-ceramics containing various amounts of CuO.

(*c*) Microprobe investigations [29] showed that copper and iron are concentrated mainly in the glassy interphase, as one may see by comparing the electron and CuKα scanning images of figs. 12a and b. The intensity distribution given in fig. 12c indicates the copper concentration as seen when crossing the grain-boundaries in the indicated direction (×) in fig 12b.

All these observations constitute strong evidence that these metallic ions act as acceptors when incorporated in the interphase.

On the other hand, there are also indications that the oxygen content, governed by the oxygen pressure at the sintering temperature, influences the resistivity anomaly of these materials, e.g. [30, 31]. As in the case of metal contacts the possibility that oxygen causes acceptor states at

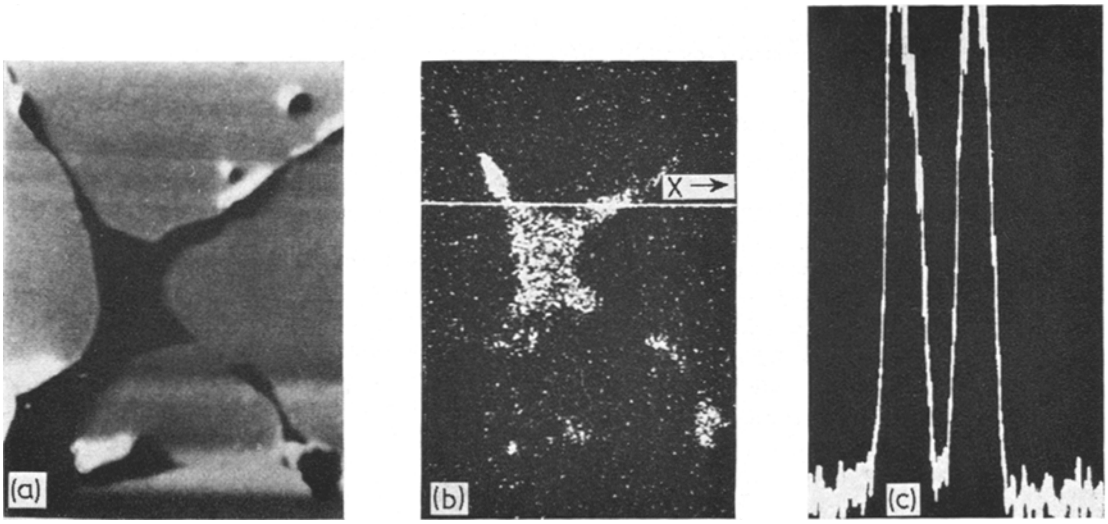

Figure 12 Detection of Cu within semiconducting $BaTiO_3$ ceramics: (a) Electron scanning microscope image. (b) CuKα emission scanning image. (c) Intensity of CuKα radiation along trace x.

interfaces cannot be excluded, but it seems more reasonable to assume that at higher oxygen pressures oxygen vacancies near the interface are avoided, which would compensate the existing acceptors.

5. Interface Barrier Capacity

As with every blocking layer, the interface barriers are not only non-linear resistances, but additionally exhibit a capacitance in parallel with this resistance. Because of the high dielectric constant of $BaTiO_3$ this capacitance acts as a short circuit at high frequencies, thus limiting the applicability of the resistance anomaly of $BaTiO_3$ to frequencies below about 100 kHz (fig. 13) [10, 23].

On the other hand one can also turn this high barrier-layer capacitance to profit, especially if the acceptor concentration is so high that ψ_0 approaches its maximum value $E_A - \zeta$ even below the Curie temperature; then one obtains very good insulating materials, as may be seen from fig. 11, curve e. The breakdown field strength E_b of these materials is high enough for many applications. Values of $E_b > 10$ kV/cm have been reached. Referring to a grain diameter of 30 μm, this corresponds to a breakdown voltage of more than 20 V per single blocking layer. This high value is mainly due to the properties of the additional interphase. Because of the small thickness of the blocking layers such artificial dielectrics can reach mean values of the dielectric constant ϵ_m up to 10^5.

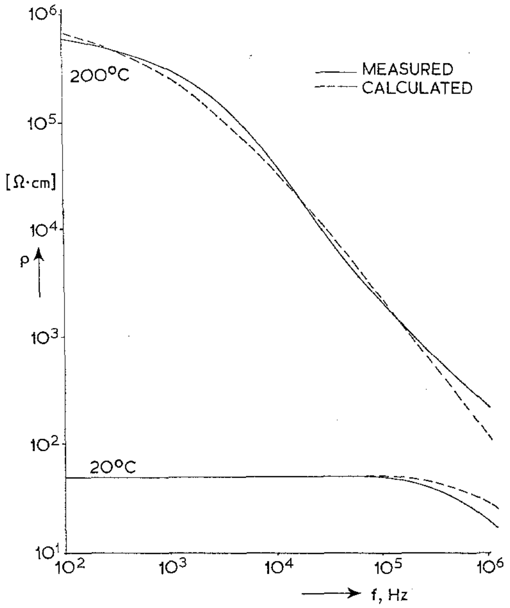

Figure 13 Dependence of resistance on frequency above Curie temperature.

The frequency-dependence of ϵ_m and of the dissipation factor tanδ are plotted in fig. 14. There is a broad minimum of tanδ at about 10^4 Hz. The increase at higher frequencies is due to the series combination of the barrier-layer capacity and the grain-bulk resistance. Thus a dissipation factor equal to 1 is reached for a frequency f_1 which is determined by

$$f_l = \frac{d}{2\pi\epsilon\epsilon_0\rho_b D} = \frac{1}{2\pi\epsilon_m\epsilon_0\rho_b} \qquad (4)$$

where ρ_b = bulk resistivity and D = grain diameter. From $f_l = 2 \times 10^6$ sec^{-1}, as found for the sample of fig. 14, one calculates a bulk resistivity $\rho_b = 15$ ohm.cm in fairly good agreement with the value found for ptc resistors having the same Sb content. The measured value of about 10 ohm.cm indicates roughly the minimum bulk resistivity reached up to now with this kind of dopant. A much lower value, of the order of 0.3 ohm.cm, must have been reached when using Dy as a dopant by Waku [32], to judge from the fact that he succeeded in shifting f_l up to 2×10^8 sec^{-1} for $\epsilon_m \approx 30000$.

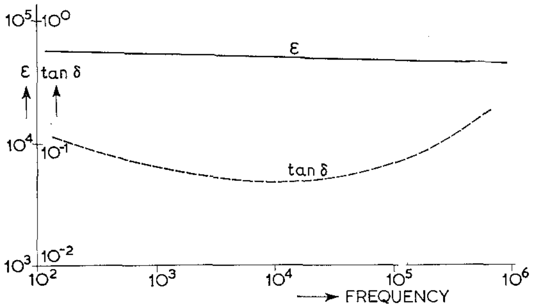

Figure 14 Dielectric constant and loss tangent of barrier layer capacitors versus frequency.

The temperature-dependence of the dielectric constant is smaller than one normally finds for undoped $BaTiO_3$. This is due to the influence of the non-perovskite interphase. Nevertheless it is appropriate to shift the Curie point to room-temperature to get very flat temperature curves, as may be seen from fig. 15.

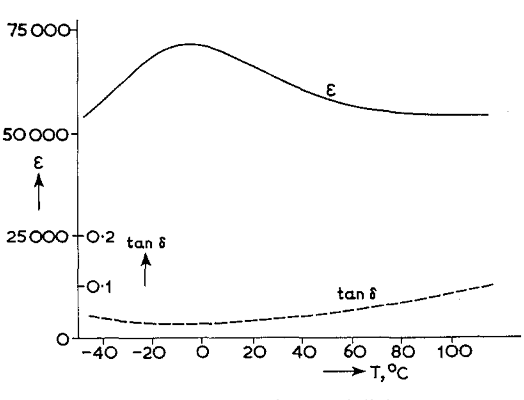

Figure 15 Temperature dependence of dielectric constant and loss tangent of Sb-doped $BaTiO_3$ barrier layer capacitors containing CuO.

6. Related Materials

The possibility of shifting the Curie temperature is even more important for the semi-conducting samples than for the capacitors, because these have already reached extensive technical application as so-called "ptc-resistors" or "cold-conductors" (Kaltleiter). As already outlined, the onset of the resistivity anomaly is directly connected with the Curie point and thus both can simultaneously be shifted to a wanted temperature by varying the composition of the material. On this basis, highly sensitive sensors for various temperature-ranges have been developed.

The methods for shifting the Curie point are well known. One uses a substitution of Ba by Pb for an increase and a substitution of Ba by Sr or Ti by Zr or Sn for a decrease of T_c. Thus one can realise substances the Curie temperatures of which range from absolute zero to about 500° C [33]. One cannot however use the whole of this range for ptc materials. Owing to the finite activation energy of the donors, of the order of 0.1 eV, the electrons in the bulk are trapped from the conduction band when the temperature becomes lower than − 30° C. Thus the bulk resistance increases very sharply with falling temperature and becomes comparable with the resistance of the blocking layers, as may be seen from fig. 16. This limits the range of interest to materials with Curie temperatures higher than about − 100° C.

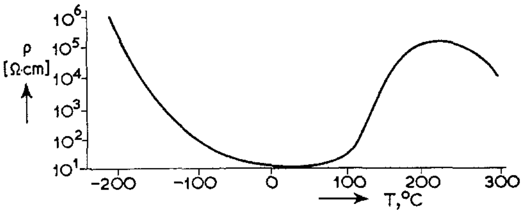

Figure 16 Increase of resistivity at low temperatures in comparison with the increase at the Curie temperature.

At the other extreme, owing to the increase of conductivity by parasitic effects with increasing temperature (well known for all types of insulating materials), materials with appreciably high resistance anomalies have been attained only when using materials with Curie temperatures below about 200° C. These parasitic effects may partially be due to a loss of lead when sintering, as for these materials, one needs lead contents of the order of 20%. The mentioned upper limit for the resistance anomaly is not a physical one. Thus one may expect a further increase by improving the materials technology.

The technical interest of this high temperature material mainly arises from its applicability for self-stabilising heating elements. If one heats such an element to its critical temperature by applying a constant external voltage, the heat-production is diminished by the resistance increase itself. This autostabilisation works for any degree of heat-removal which is smaller than the heat-production below the critical temperature.

The substitutions used for the Curie shift have always the same valency as the substituted ions, whereas the dopants needed to maximise the resistance anomaly exhibit a higher valency. But it must be emphasised that the substitution normally concerns the same lattice sites. Thus one may expect an interference between these two effects, mainly influencing the doping action because of the small amounts used. This interference can be minimised if one uses different lattice sites for Curie shift and doping, e.g. a substitution of Ti^{4+} by Zr^{4+} for the shift and a substitution of Ba^{2+} by Sb^{3+} for the doping. Resistance temperature characteristics for a set of semiconducting materials produced by these methods are shown in fig. 17.

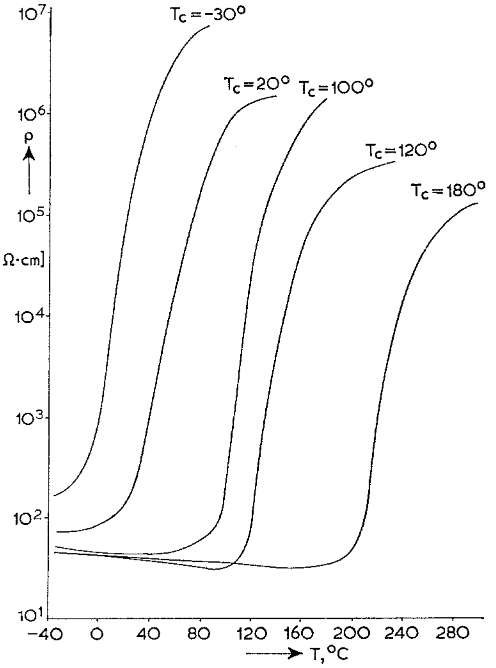

Figure 17 Ptc-characteristics of ceramics with different Curie temperatures.

7. Conclusion

The interest in semiconducting $BaTiO_3$ arose about fifteen years ago because of the surprising resistance anomaly. With the increasing understanding of this effect it has been possible to develop a new type of material with a very large versatility. It can be expected that the technical interest will further increase because it is now possible to make really tailor-made materials adapted in temperature and voltage characteristics to a large range of applications.

Acknowledgement

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References

1. R. C. CASELLA and S. P. KELLER, *Phys. Rev.* **116** (1959) 1469.
2. O. SABURI, *J. Amer. Ceram. Soc.* **44** (1961) 54.
3. P. GERTHSEN, R. GROTH, K. H. HÄRDTL, D. HEESE, and H. G. REIK, *Solid State Commun.* 3 (1965) 165.
4. P. GERTHSEN, R. GROTH, and K. H. HÄRDTL, *Phys. Stat. Sol.* **11** (1965) 303.
5. H. IKUSHIMA and S. HAYAKAWA, *Jap. J. Appl. Phys.* **4** (1967) 454.
6. C. N. BERGLUND and W. S. BAER, *Phys. Rev.* **157** (1967) 358.
7. S. IKEGAMI and I. UEDA, *J. Phys. Soc. Japan* **19** (1964) 159.
8. H. IKUSHIMA and S. HAYAKAWA, *Jap. J. Appl. Phys.* **4** (1967) 328.
9. H. BRAUER, *Z. angew. Phys.* **23** (1967) 373.
10. W. HEYWANG, *J. Amer. Ceram. Soc.* **47** (1964) 484.
11. B. A. ROTENBERG, YU. L. DANILYUK, E. I. GINDIN, and V. G. PROKHATILOV, *Fizika Tverdogo Tela* **7** (1965), 3048; *Sov. Phys. Solid State* **7** (1966) 2465.
12. G. H. JONKER, *Sol. State Electron.* **7** (1964) 895.
13. H. SCHMELZ, *Phys. Stat. Sol.* **35** (1969) 219.
14. E. C. SUBBARAO and G. SHIRANE, *J. Amer. Ceram. Soc.* **42** (1959) 279.
15. O. EBERSPÄCHER, *Naturwiss.* **49** (1962) 155.
16. H. SCHMELZ, *Phys. Stat. Sol.* **31** (1969) 121.
17. W. HEYWANG, *Ferroelectrics* **1** (1970) 177.
18. T. MURAKAMI, *Rev. Electr. Commun. Lab.* **16** (1968) 551.
19. H. SEITER, private communication; see also W. HEYWANG, *Festkörperprobleme* **6** (1967) (Vieweg & Sohn, Braunschweig) p. 66.
20. H. A. SAUER and S. S. FLASCHEN, *Amer. Ceram. Soc. Bull.* **39** (1960) 304.
21. L. HANKE, *Nachr. Fachberichte* **29** (1964) 51.
22. W. HEYWANG, *Sol. State Electron.* **3** (1961) 51.
23. *Idem*, *Z. angew. Phys.* **16** (1963) 1.

24. *Idem*, *Ber. deutsch. Keram. Ges.* **47** (1970) 674.
25. W. HEYWANG and H. BRAUER, *Sol. State Electron.* **8** (1965) 129.
26. P. GERTHSEN and K. H. HÄRDTL, *Z. Naturforsch* **18a** (1963) 423.
27. H. REHME, *Phys. Stat. Sol.* **18** (1966) K 101.
28. *Idem*, *Z. angew. Phys.* **29** (1970) 173.
29. *Idem. Phys. Stat. Sol.* **26** (1968) K 1.
30. I. UEDA and S. IKEGAMI, *J. Phys. Soc. Japan* **20** (1965) 546.
31. T. ASHIDA and H. TOYODA, *Japan. J. Appl. Phys.* **5** (1966) 269.
32. S. WAKU, *Rev. Electr. Commun. Lab.* **15** (1967) 689.
33. H. BRAUER and E. FENNER, *Keram. Z.* **12** (1964) 766.

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