

Electric Breakdown of Barium Titanate: A Model

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Abstract. A model is proposed to explain observations on electric breakdown of BaTiO₃ ceramics: Ceramics made by usual sintering technique contains TiO₂-rich intermediate layers between the grains of the polycrystalline structure. Field inhomogeneities are shown to result, with the field enhanced by factors of up to 100 or more in places. The very high field strength ensuing when the applied test voltage approaches its breakdown value causes inner field emission, with currents abruptly rising to very high values and thermally destroying the sample at once.

Index Headings: Electric breakdown – Barium titanate

Barium titanate ceramics is characterized, besides by a very high permittivity ϵ that makes it useful for many applications, by a rather low breakdown field strength that often diminishes its usefulness. (Measured values: 100...180 kV/cm [1–5]).

To investigate dc breakdown, the author has examined the dependence of dc breakdown field strength on the electrode material, sample thickness, sintering technique (sintering at atmosphere pressure – hot pressing), and temperature – a detailed account on the experiments was given in [5, 6] – and now proposes a model of the breakdown mechanism that explains the experimental results as well as the coincidence of high ϵ and low breakdown strength.

1. Experimental Results

The “normally sintered” ceramics used here were sintered in oxygen atmosphere at normal pressure (atmospheric pressure) at temperatures gradually rising up to 1430° C. For means of comparison and, moreover, for part of the measurements of thickness

dependence specimens isostatically hot pressed at about 1250° C [26]¹ were used.

Only electric breakdown was investigated; values brought about by thermal breakdown were cancelled, because thermal breakdown is no mere property of matter.

The experiments yielded the following results:

Breakdown strength E_b is

— of the order of $1.5 \cdot 10^2$ kV/cm at room temperature,

— independent of electrode material,

increased at low temperatures (factor of 1.5...2 by cooling from room temperature to liquid air temp.), hence

— increased with decreased ϵ (ϵ at liquid air temp. is smaller by a factor of 2 than it is at room temp.), and

— breakdown is not of avalanche type (for the avalanche breakdown field is known to decrease with decreasing temperature [7, 8, 22], with ϵ temperature independent and all the more with decreasing ϵ).

As a second test on avalanche breakdown, the thickness dependence of E_b was investigated, thicknesses

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ranging down to 20 μm , – with the same finding: no thickness dependence, whereas avalanche breakdown should yield increasing strength with decreasing thickness [24].

— E_b of the hot pressed specimens is higher by a factor of 3...4, thus being in the order of magnitude of single crystals (cf. [10–12]).

This effect of hot pressing cannot be explained merely by the reduction of porosity (from 2% to 0%, concerning the samples of this investigation): According to [13, 14] this reduction should cause an increase in strength of not more than ca. 20%.

2. The Model Proposed

2.1 A Survey

In normally sintered ceramics as produced by the procedure described above, intermediate layers between the grains have been proved, consisting of BaTi_3O_7 + contaminants [15, 16]. They originate from a liquid sinter phase existent above 1322°C [17] and have thicknesses of up to 1 μm in places. – Consider, in a sample under high voltage test, the part of such a layer which is oriented perpendicular to the field direction. As the magnitude of permittivity ϵ is a few tens in BaTi_3O_7 [18], but more than thousand in the BaTiO_3 grains, field strength in the layer is enhanced by a considerable amount. A more exact estimation to be stated below yields a factor of about 100 in places.

Thus field strengths of about $1.5 \cdot 10^4$ kV/cm will be reached in those places as soon as the mean field strength E_{av} of the sample reaches the breakdown value of $1.5 \cdot 10^2$ kV/cm. These values are already in the order of the onset field strength of inner field emission, causing considerable emission current that will rise steeply with further increase of field strength, and will thermally destroy the sample at once.

2.2 Consideration of the Details

2.2.1 Field Enhancement in the Intermediate Layer

A part of the layer oriented perpendicular to field be considered together with the two adjacent grains, at large applied field strengths ($E_{av} \gg$ coercitive field of BaTiO_3).

With superscripts G, L for terms in the grain and layer, respectively, we have in the grains

$$D^G = \epsilon_0 \cdot E^G + (P^G - P_s) + P_s \quad (1)$$

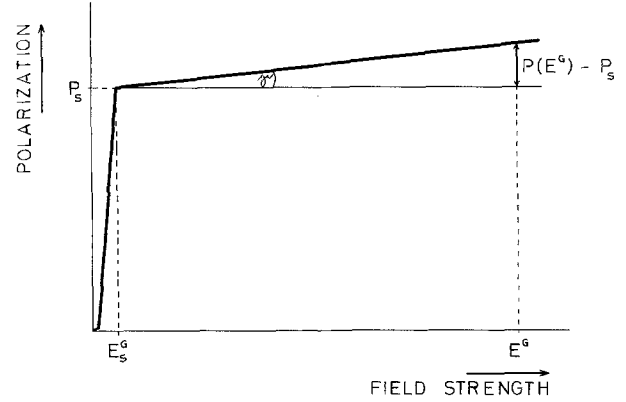


Fig. 1. Initial polarization curve of a ferroelectric as BaTiO_3 (schematic). $P(E^G) - P_s = \tan \gamma \cdot (E^G - E_s^G) \approx \tan \gamma \cdot E^G$
 $\tan \gamma$ is ϵ_0 times the differential susceptibility at high fields, hence ϵ^G in (2) is the differential permittivity at high fields

(D : electric displacement, P : polarization, P_s : spontaneous polarization in the grain),

$$P^G - P_s = \epsilon_0 \cdot (\epsilon^G - 1) E^G, \quad (2)$$

ϵ^G being approximately equal to the differential permittivity at high fields, as can be seen from Fig. 1.

Using (1) and (2) we get for the components parallel to $E_{av} \approx E^G$ (subscript $_{\parallel}$)

$$D_{\parallel}^G = \epsilon_0 \epsilon^G \cdot E^G + q \cdot P_s. \quad (3)$$

The factor q is dependent on the angle between field and crystallographic c -axes (=directions of P_s) which can have values of $0 \dots \arccos(1/\sqrt{3})$. Therefore $1 \geq q \geq 1/\sqrt{3}$.

Strictly speaking, ϵ^G is anisotropic, with tensorial components ϵ_c, ϵ_a belonging to the crystallographic c -direction (parallel to P_s) and the a -direction, respectively, and $\epsilon_c \ll \epsilon_a$. To take this into account, it is only necessary to consider the case of the largest field enhancement (because of the large number of randomly oriented grains, in every sample, this case will certainly be approximated in some places), namely, the direction of the space diagonal of the crystallographic unit cell of the adjacent grain being parallel to E^G . Then the angle α between E^G and the a -direction is $\arccos(1/\sqrt{3}) \approx 54^\circ 50'$.

With subscript a for components in a -direction it holds

$$D_a^G = \epsilon_0 \cdot \epsilon_a^G \cdot E_a^G + q \cdot P_s. \quad (3a)$$

$E_a^G = E^G \cdot \cos \alpha$; $D^G \approx D_a^G \cdot \cos \alpha$ (the additive contribution of the component D_c^G in c -direction has been neglected as $\varepsilon_c \ll \varepsilon_a$),

hence

$$D^G \approx \varepsilon_0 \cdot \varepsilon_a^G \cdot \cos^2 \alpha \cdot E_a^G + q \cdot P_s. \quad (3b)$$

Considering anisotropy of ε we therefore have to define ε^G by $\varepsilon_a^G \cdot \cos^2 \alpha$ ($= \varepsilon_a^G/3$). For simplicity the term ε^G shall be maintained.

In the layer we simply have

$$D^L = \varepsilon_0 \cdot \varepsilon^L \cdot E^L, \quad (4)$$

as the layer is not ferroelectric.

Setting $E_{av} \approx E^G$ (which is reasonable as the mean thickness of the layers is so small that even with $E^L = 100 E^G$ the voltage across them may be neglected in estimating the order of E^G) and $D_{\parallel}^G = D_{\parallel}^L$ (components of D normal to the boundary) we get

$$E^L \approx \frac{\varepsilon^G}{\varepsilon^L} \cdot E_{av} + q \cdot P_s / \varepsilon_0 \varepsilon^L. \quad (5)$$

This result, yielding $E^L > 10^4$ kV/cm, if $E_{av} = 1.5 \cdot 10^2$ kV/cm and $\varepsilon^G/\varepsilon^L = 100$, has to be corrected in several respects:

1) Surface traps at the layer-grain-interface, with densities of about 10^{14} cm $^{-2}$ [19, 20] will be filled up by the charges set free by inner field emission in the layer. Their surface charge ($\approx 10^{-5}$ Cb/cm 2) will then give rise to an opposing field of the same order of magnitude as the term $qP_s/\varepsilon_0 \varepsilon^L$ of (5) ($P_s = 2.6 \cdot 10^{-5}$ Cb/cm 2). The resulting field E_r of both will thus be of the order of some 10^3 kV/cm or less.

2) ε^G , ε^L are permittivities under high bias field. Measurements with a bias field higher than 24 kV/cm have not yet been made with BaTiO $_3$. A lengthy consideration for which we have to refer to [5] yielded an estimation of 20...30 for $\varepsilon^G/\varepsilon^L$.

3) Unevennesses (projections) of the layer-grain boundary give rise to local field enhancement in the layer. An estimation using Schottky's hemisphere approximation [21] yielded an enhancement factor g of order of 3...10 [5].

So the enormously high field strengths mentioned above are restricted to very small areas: the vicinities of appropriate projections of appropriate grains. For those the field strength is finally

$$E^L = g \cdot \frac{\varepsilon^G}{\varepsilon^L} \cdot E_{av} + E_r, \quad E_r \lesssim 10^3 \text{ kV/cm} \quad (6)$$

$\approx 100 E_{av}$ as an order of magnitude estimate.

2.2.2 Field Emission

The emitted current was calculated after Franz [23], who gives a relation of Fowler-Nordheim type

$$I(E) \sim E^{10/3} \cdot \exp\left(-\text{const} \frac{w^{3/2}}{E}\right), \quad (7)$$

where w denotes the band gap. Characteristic for this relation is a rather abrupt increase of current from formerly negligible values when an "onset field strength" is exceeded, with an order of magnitude increase of current caused by a further field increase of a few percents.

The calculation (as well as all the following) was based on the assumption of an emitting volume (= volume of highest field) of $(0.05 \mu\text{m})^3$. – For the onset field strength we found a value a little below $1.5 \cdot 10^4$ kV/cm, e.g. $1.45 \cdot 10^4$ kV/cm yielding a current of 20 μA .

In addition to field emission, impact ionisation by the emitted charge carriers may occur. It does not play the dominant role (as is shown by the experimental results: no avalanche breakdown) because the very high field strength is restricted to very small areas.

2.2.3 Retroaction of the Emitted Charge

The charges of the emitted carriers are not compensated by stationary charges of opposite sign (e.g., ionized impurities). So their space charge causes an additional field that diminishes the original one at the emitting area, by an amount ΔE . In order to estimate ΔE , the current path in the "first" layer, i.e. the layer comprising the emitting area, was approximated by a cone of 90° aperture angle. (By the way, the widening of current path is governed mainly by diffusion of the charge carriers, the effect of mutual repulsion is negligible in comparison.) Accordingly the part of ΔE that is due to space charge within the cone was calculated to be less than $1.5 \cdot 10^3$ kV/cm if

$$I = 20 \mu\text{A}$$

$$\varepsilon^G \approx 1000$$

$$\frac{\varepsilon^G}{\varepsilon^L} = 25$$

$$v_{Dr} \text{ (drift velocity of carriers)} \geq 10^6 \text{ cm/sec.}$$

The – unknown – value of drift velocity in the layer was taken quite small for safety reasons: Larger values of v_{Dr} will give smaller ΔE 's.

The effect due to the rest of the space charge in the sample can be neglected compared to the contribution of the first layer, no matter how the current path may be shaped. So, the whole ΔE can still be neglected compared to the total field strength at the emitting area.

2.2.4 Sample Heating and Destruction

With current rising to considerable values the temperature along the current path increases strongly, particularly in the layer where the field strength is enhanced. It was calculated that a current of $20 \mu\text{A}$ will heat up the cone in the first layer to the melting temperature (1600°C) within microseconds.

Calculation: For the case of heat being generated at a given rate in a cylindrical area of an infinite medium during a given time, the rise of temperature in the axis of the cylinder was calculated [9]. This case, with dimensions of the cylinder taken equal to the dimensions of the current path within the "first" layer, seemed to be a good estimate, the boundary conditions comprised are justified because the cylindrical area is small compared with the whole sample and is heated up within few microseconds.

As the material is melting, field emission is superposed or replaced by field enhanced thermal emission from the melt. Saturation current density for this case of emission from melt to the adjacent solid of the same material, at a field strength of $1.5 \cdot 10^2 \text{ kV/cm}$ was calculated to be of the order of several 10^4 A/cm^2 (see [25, 5]). This is enough to melt the current path through the grains, too, during few microseconds. Thus a conducting melt channel is produced – the sample is broken down.

3. Comparison with Experiment

The model presented is able to explain all the experimental observations reported: It obviously demands that the breakdown field

— is independent of electrode material: breakdown starts from layers within the sample

— increases with decreased ϵ of the BaTiO_3 : see (6)

— and that there is no avalanche breakdown.

What about the isostatically hot pressed specimens? In contrast to the normally sintered ceramics used in this work, there have not been found surface layers in the hot pressed material used, certainly because of the special sintering technique with sintering temperature well below 1322°C , below which temperature there is no liquid sinter phase. (There are layers reported in ceramics hot pressed

by other techniques using temperatures above 1322°C !) Thus the mechanism of the model cannot work, and breakdown cannot take place – until at higher field strengths another mechanism will start. The same holds for single crystals where, off course, there are no layers either, so it is well understandable that breakdown fields in the isostatically hot pressed specimens are of the same order as in single crystals.

Finally, the question of a correlation between high permittivity ϵ and low breakdown strength of ceramics can be answered plainly: There is a relation, low strength is conditioned, however, not simply by high ϵ but by concurrence of such an ϵ and appropriate layers between the grains, as is the case in normally sintered BaTiO_3 ceramics.

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