

## A study of the dielectric properties of powdered BaTiO<sub>3</sub>

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Received 19 December 1972, in final form 23 July 1973

**Abstract.** The anomalous behaviour of powdered barium titanate is confirmed by the use of the formula for mixtures. Systematic measurements of the dielectric properties of BaTiO<sub>3</sub> have been done for two cases: embedded grains and fine-grained pressed powder. The influence of the size and shape of the grains, and of the method of preparation of the samples, has been studied.

### 1. Introduction

Barium titanate has been known for a long time as a ferroelectric material. However, it is still used for the study of ferroelectricity because of its interesting properties: single crystals or ceramics can be obtained with this material; its crystalline structure is relatively simple; it is ferroelectric at room temperature; the temperature of the transition between ferroelectric and paraelectric phases is not too high (121 °C).

If the particles are very small, it has an anomalous behaviour, and explanations are different from one author to another. In order to investigate the effect of the size of the particles, we have done calorimetric and dielectric measurements with particles ranging from 1 µm to 1 mm.

The powders have been made by grinding ceramics and sorting with sieves or with a centrifugal process.

### 2. Calorimetric measurements

We repeated previous measurements done in the laboratory (Richard *et al* 1962) with a larger number of samples. The apparatus used in the present study has been described in a previous paper (Richard 1963).

The results obtained for the enthalpy variation at the transition between ferroelectric and paraelectric phases are summarized in figure 1. They confirm our previous results. The absorbed energy decreases with the size of the particles. This decreasing begins with particles of 40 µm, and the energy is practically zero below 3.5 µm.

### 3. Dielectric measurements

With a General Radio automatic capacitance bridge we measured the permittivity of barium titanate on various samples: pressed powder; pressed powder heated at a temperature lower than the temperature of sintering; powder mixed with styrene. The frequency of the applied electric field was 1000 Hz and its amplitude was a few volts.

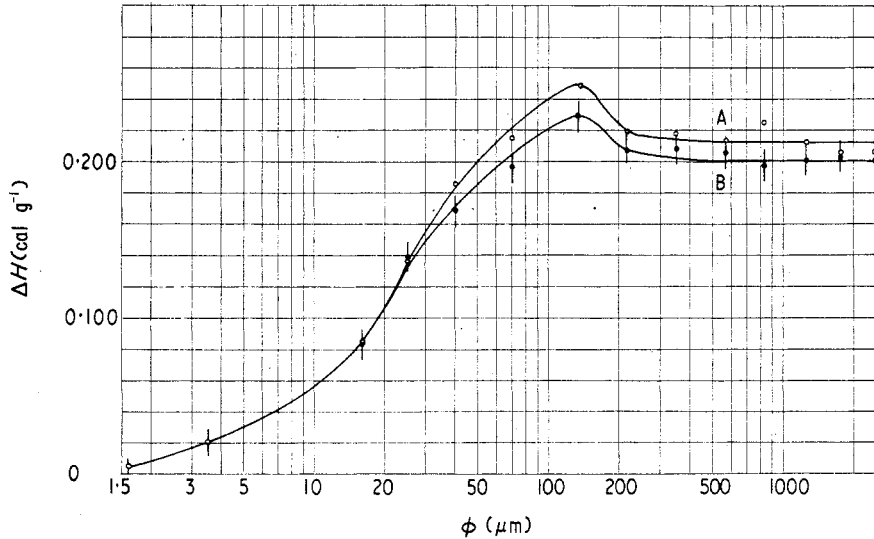


Figure 1. Variation of enthalpy ( $\Delta H$ ) with the size of the grains: A, lowering of temperature; B, raising of temperature.

### 3.1. Pressed samples

For the dielectric measurements we deposited metallic electrodes, and therefore the samples had to be rigid enough. It was possible to get such samples only with particles of 1  $\mu\text{m}$  and a volume concentration of about 60%.

With the formula for the dielectric constant of mixtures that we already proposed (Paletto 1966, Paletto *et al* 1966)

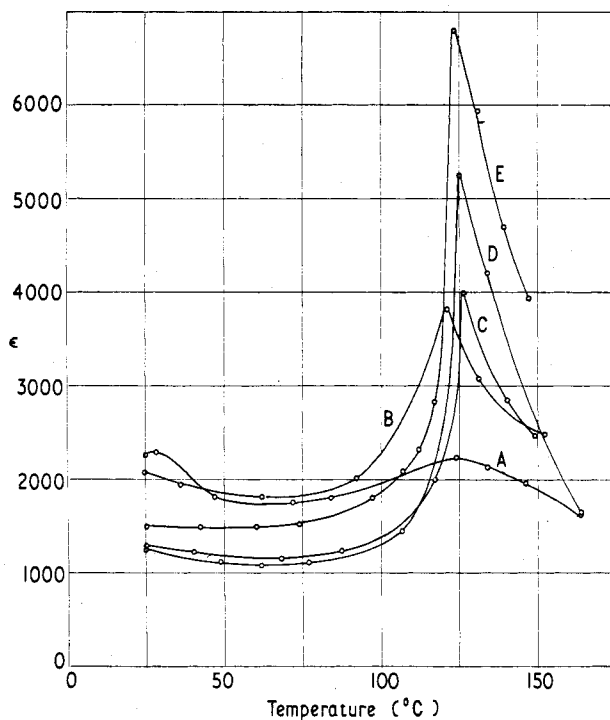
$$\xi_m = (1 - \delta) \frac{9\delta\xi_2 + (\xi_2 + 2)^2 (1 - \delta)}{[(\xi_2 + 2)(1 - \delta) + 3\delta]^2} + \delta \frac{9(1 - \delta)\xi_2^2 + (1 + 2\xi_2)^2 \delta\xi_2}{[(1 + 2\xi_2)\delta + 3\xi_2(1 - \delta)]^2}$$

(where  $\xi_2 = \epsilon_2/\epsilon_1$  is the reduced permittivity of the small spherical particles and  $\delta$  is the volume concentration of particles), we calculated a permittivity of about 150 for BaTiO<sub>3</sub>. This result is in good agreement with that one deduced, with the preceding formula, from the measurements of Goswami (1969) on fine-grained pressed powder, the volume concentration of which was about 62%.

### 3.2. Pressed and heated at 1200 °C samples

Many authors (eg Richard 1963, Goswami 1964) have noted that in a ceramic the mean diameter of particles is a function of temperature and of the period of sintering. Particles do not change for one hour at 1200 °C. We made a line of samples heated at 1200 °C from powder composed of particles of different sizes. We checked with a microscope that the diameter of the particles had not increased. The porosity of each sample ranged between 20 and 25%. We deposited metallic electrodes and then measured their permittivity. After computing with the formula for mixtures we plotted the curve (figure 2) of the permittivity of BaTiO<sub>3</sub> against the temperature for different sizes of particles.

This curve shows that for very small particles the ferro–paraelectric transition disappears, and that the temperature of the antiferro–ferroelectric transition increases.



**Figure 2.** Variation of permittivity with temperature for 'presintered' samples obtained from powder of different-sized grains: A,  $\phi < 1.3 \mu\text{m}$ ; B,  $1.3 < \phi < 6.6 \mu\text{m}$ ; C,  $6.6 < \phi < 18 \mu\text{m}$ ; D,  $18 < \phi < 26 \mu\text{m}$ ; E,  $26 < \phi < 50 \mu\text{m}$ .

These results are in good agreement with those of Kiss *et al* (1966). As the diameter of the particle increases, the curve tends to that of a normally sintered ceramic.

### 3.3. Powder mixed with styrene samples

The binding medium used was liquid styrene, which polymerized with a catalyst (about 1% of benzoyl peroxide) at 60 °C for at least 24 h. In order to carry out measurements against temperature we added 30% of divinylbenzene; the softening point was then about 200 °C.

Styrene and powder were stirred well in a cup made of Teflon, and the whole was put into a stove. After polymerization, we polished the samples. Then we computed the volume concentration assuming that the porosity is zero.

The measurements were done with samples whose volume concentration ranged from 30 to 60%. At higher values the particles begin to touch one another.

The results are summarized in table 1. They show that whatever the size of the particles, the permittivity of BaTiO<sub>3</sub>, at room temperature, computed from experimental measurements with the proposed formula, is low compared with the permittivity of a BaTiO<sub>3</sub> sintered ceramic. Errors in measurements and utilization of the formula are about 10%.

**3.3.1. Influence of the form of the particles.** We used spherical particles ( $0.99 < \phi < 1.48 \text{ mm}$ ) and small cubic particles (1 mm of side). Before mixing cubic particles, we measured the

**Table 1.** Permittivity, measured at room temperature, of powdered BaTiO<sub>3</sub>, computed with the formula proposed by the authors for different sizes of particles

Diameter of the grains	Volume concentration	$\epsilon_m$	$\epsilon$ deduced from $\epsilon_m$	Mean value of $\epsilon$
$\phi < 1.3 \mu\text{m}$	22	8.2	202	195
	61	53.2	190	
$1.3 < \phi < 6.6 \mu\text{m}$	38	15.7	146	150
	39	14.8	123	
	58	41.9	163	
	66	53.8	156	
	67	59.4	166	
$6.6 < \phi < 18 \mu\text{m}$	42	18.5	140	135
	44	18.7	130	
$18 < \phi < 26 \mu\text{m}$	40	12.5	92	92
	40.5	12.7	93	
$26 < \phi < 50 \mu\text{m}$	48	16.1	90	88
	54.5	19.8	82	
	55	20.8	90	
	56.5	25	90	
$50 < \phi < 90 \mu\text{m}$	42	13	92	90
	43	13.3	82	
	44	14.3	95	
	60	28.7	90	
$90 < \phi < 180 \mu\text{m}$	46	15	90	92
	49	17.1	94	
$0.18 < \phi < 0.25 \text{ mm}$	40	12.6	93	96
	46	15.3	99	
$0.25 < \phi < 0.45 \text{ mm}$	38	11.5	93	94
	41	13	99	
	46	15.7	89	
$0.45 < \phi < 0.69 \text{ mm}$	55.5	35.5	151	135
	56	28.6	118	
$0.69 < \phi < 0.99 \text{ mm}$	58	49.4	197	197
$0.99 < \phi < 1.48 \text{ mm}$	51	36.4	194	205
	56	46.1	202	
	57.5	56.8	227	
	58.8	50.8	197	

variation of the permittivity of one particle against temperature, and the results are practically the same as for a ceramic (figure 3). After mixing, the results are the following: cubic grains percentage 59 %, permittivity 215; spherical grains percentage 56 %, permittivity 202. In both cases there is no variation of permittivity with temperature. Permittivity does not depend on the shape of the grains when they are embedded.

**3.3.2. Influence of the preparation of samples.** With middle-sized powder ( $26 < \phi < 50 \mu\text{m}$ ) we made three samples in different ways: by embedding grains in liquid styrene, when

the percentage is 59%; (ii) by pressing powder and pouring styrene over it, when the grains touch one another and the percentage is 62%; (iii) by heating pressed powder at 1200 °C for one hour and pouring styrene over it, when the percentage is 79%.

In the three cases we plotted the variation of the permittivity of BaTiO<sub>3</sub>, computed with the proposed formula, against temperature (figure 4). We note that permittivity is low and independent of temperature for embedded particles. To check that these embedded particles are still in the ferroelectric phase we recorded, at room temperature, the x-ray diffraction diagrams of a powder and of embedded grains (figure 5).

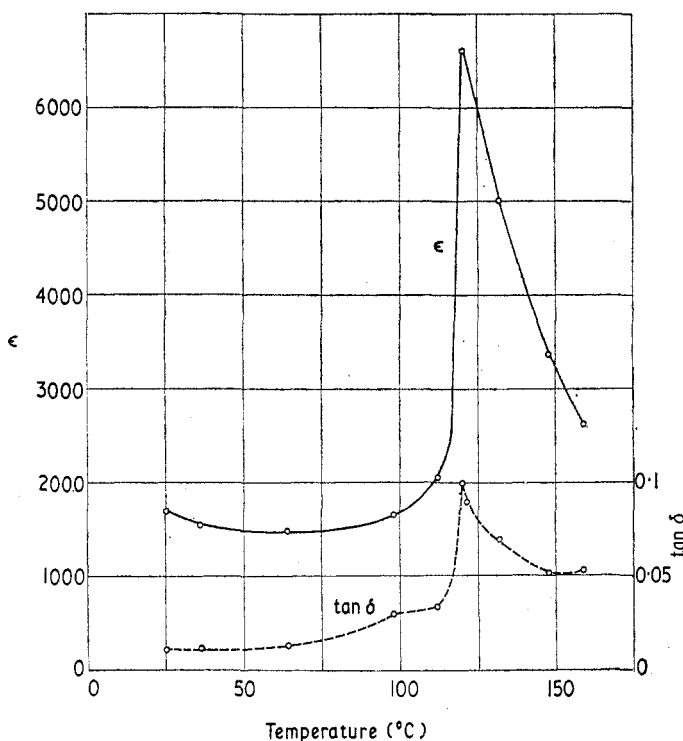


Figure 3. Variation of permittivity and of  $\tan \delta$  of a cubic particle (1 mm of side) with temperature.

In both cases the diagram presents the lines (330-303-114) corresponding to the tetragonal structure of BaTiO<sub>3</sub>. For the second sample, at room temperature, we find the value of  $\epsilon$  of a ceramic, but at the Curie temperature the value is lower. For the sample (iii) we find the same value as for a ceramic.

#### 4. Conclusions

This study shows that:

- (i) The transition energy decreases with the diameter of the grains.
- (ii) At room temperature the permittivity of the sample obtained from a fine-grained pressed powder is low.
- (iii) The permittivity of a sample which has been 'presintered' from a fine-grained pressed powder is high and constant with temperature.

(iv) The permittivity of grains, computed with the above-mentioned formula for the dielectric constant of mixtures, is low, because the grains are embedded in a nonpolar solvent.

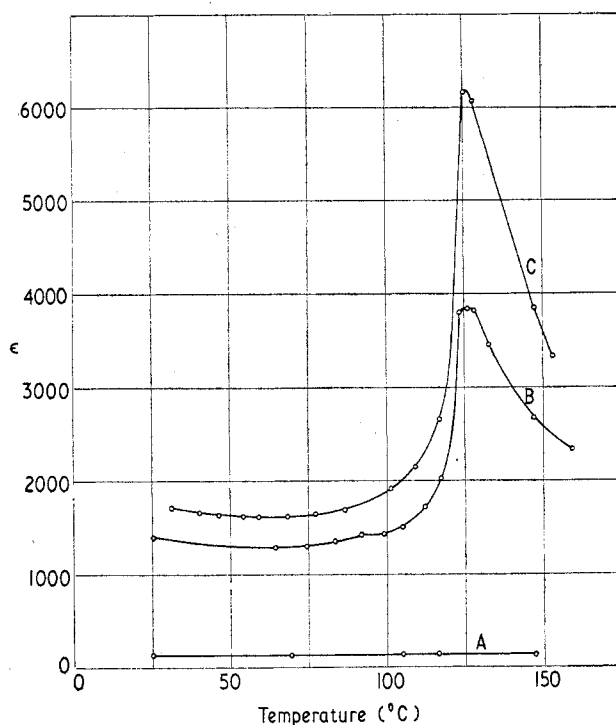


Figure 4. Variation of permittivity, computed with the formula for mixtures, with temperature for different samples of  $\text{BaTiO}_3$ . These samples have been made with powder of diameter  $26 < \phi < 50 \mu\text{m}$ , mixed with styrene in different ways: A, powder mixed with styrene; B, pressed powder + styrene; C, 'presintered' powder + styrene.

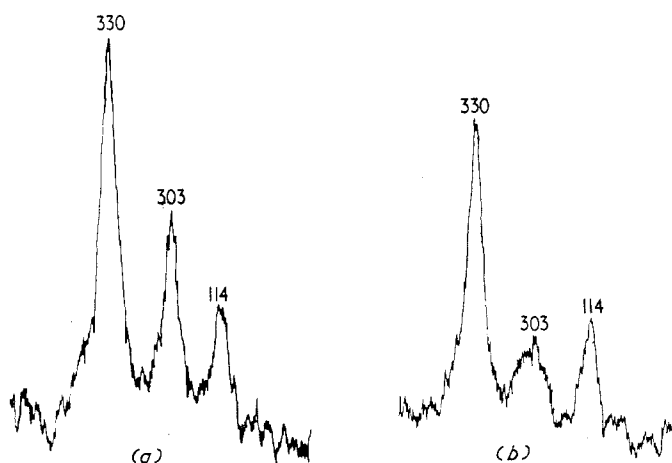


Figure 5. Diffraction diagrams, at room temperature, of (a) grains of diameter between 26 and  $50 \mu\text{m}$ , and (b) grains of the same diameter embedded in styrene.

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