JOURNAL OF MATERIALS SCIENCE 7 (1972) 339–343

Energy Storage in Ceramic Dielectrics

I. BURN, D. M. SMYTH*
Sprague Electric Company, North Adams, Massachusetts 01247, USA

An evaluation has been made of the energy storage capabilities of ceramic dielectrics that were considered likely to provide high energy/volume efficiency on the basis of their expected permittivity-field characteristics. Data for fields up to 400 kV/cm are presented for a strontium titanate, and for a barium titanate ceramic. The materials were in thick-film form and bonded with a small amount of glass. At the maximum fields, energy storage in the barium titanate ceramic was close to that reported earlier for glass-bonded lead zirconate (approx. 2.0 J/cm^3), but was about 30% lower in the strontium titanate material.

1. Introduction

The energy stored per unit volume of a dielectric, J, is given by

$$J = \int_0^{D_{\max}} E \, \mathrm{d}D \qquad (1)$$

where E is the electric field and $D_{\max}$ is the electric displacement (D) at the highest field applied ($E_{\max}$). Also, since the permittivity (ϵ) is defined as $\mathrm{d}D/\mathrm{d}E$,

$$J = \int_0^{E_{\max}} \epsilon \, E \, \mathrm{d}E \qquad (2)$$

Thus, the highest attainable stored energy per unit volume of a given dielectric can be obtained from equation 2 by substituting the breakdown field for $E_{\max}$ and the permittivity as a function of field for ϵ. Fig. 1 shows schematically the form of the dependence of D on E for the usual types of dielectric and also the corresponding dependence of permittivity on field. For dielectrics of high relative permittivity (i.e. $\epsilon/\epsilon_0 \gg 1$), D can be replaced by the polarisation. As pointed out by Jaffe [1], the shaded areas represent the available energy per unit volume of dielectric on discharge.

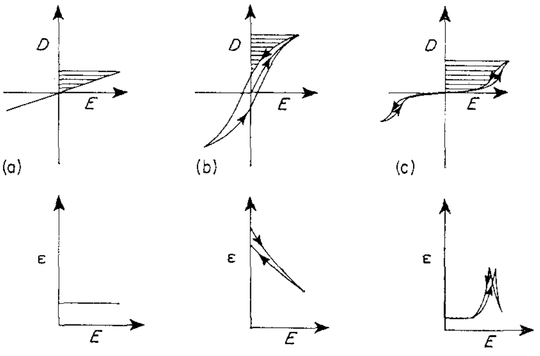

Figure 1 Typical dependence of electric displacement and of permittivity on field for (a) linear, (b) ferroelectric, and (c) antiferroelectric ceramics.

Although the dielectric characteristics that are suitable for high energy storage are quite well recognised [1, 2], quantitative information on the energy storage capabilities of ceramics is sparse and in the past has generally been limited to fields less than 150 kV/cm. This is because of the relatively low dielectric strength of ceramics when in the form of sintered pressed disks [2, 3, 4]. In an earlier paper [5], however, energy storage measurements on lead zirconate, an antiferroelectric, were reported for fields up to 400 kV/cm; thick-film techniques were employed and the ceramic was bonded with a small amount of low-softening-point glass. This approach was also used in the present work in which energy storage measurements at high fields were made on ceramic materials with dielectric properties representative of types (a) and (b) in fig. 1. These were (i) strontium titanate, a material generally regarded as linear (at least for the fields commonly encountered in practice), and

---

*Present address: Materials Research Center, Lehigh University, Bethlehem, Pennsylvania 18015, USA.

(*ii*) a barium titanate ceramic with a broad Curie peak and thin hysteresis loop.

2. Experimental

2.1. Materials

The strontium titanate was Ticon S*, a commercial electronic ceramic. It was found to contain 0.7 Ba, 0.3 Ca and 0.2 to 0.3 wt % Si as major impurities. The barium titanate ceramic was a capacitor dielectric composition containing approximately 95% $BaTiO_3$ with additives to minimise the dependence of the permittivity on temperature. Without a glass binder this material has a relative permittivity of 2000 ± 200 over the range − 55 to 125° C.

To each ceramic was added approximately 10% glass powder by (true) volume as a binder. The binder for the barium titanate ceramic was a borosilicate composition, containing Bi_2O_3 and PbO similar to that used in the work on lead zirconate [5, 6]. A glass of composition $4\,BaO.Al_2O_3.2\,B_2O_3$ [7] was used for the strontium titanate, since glasses containing lead or bismuth were unsuitable as they tended to lower the resistivity of the material.

Thick-film capacitors were prepared by a screen-printing technique as described earlier [5]. Units containing the $SrTiO_3$ were fired at 1250°C for 1/2 h and those containing the $BaTiO_3$ ceramic at 1120°C for 1 h.

2.2. Electrical Measurements

Since the energy storage per unit volume of dielectric is given by equation 2, the energy can be predicted if the variation of the permittivity with field can be measured. If, at a given field, the displacement for increasing and decreasing fields is the same, or not very different, i.e. if there is little or no hysteresis, then the dependence of the permittivity on field can be determined by measuring the capacitance with a small AC signal superimposed on a DC bias which is gradually changed. Capacitance measurements were made using a 1 V, 1 kHz signal. Bias was applied with a 2.5 kV-2 mA DC power supply with the bridge protected by a 10 MΩ resistor and a 1 μF blocking capacitor. To convert capacitance readings to permittivity values a geometry factor for each type of capacitor was determined by preparing polished sections of several units and making measurements of electrode area and dielectric thickness.

For materials that exhibit hysteresis, the dependence of the permittivity on field is not easily obtained since a small signal measurement can be appreciably lower than the true differential value (dD/dE) [8]. For the barium titanate ceramic, therefore, direct measurements of energy storage were made by a pulse discharge technique [5] as a check.

3. Results and Discussion

3.1. Strontium Titanate

Measurements of permittivity versus DC bias for strontium titanate bonded with barium aluminoborate glass are shown in fig. 2a. Some decrease in permittivity at high fields is to be expected and the departure from linearity can be expressed by extra terms in a power series relating D and E, viz

$$E = \alpha D + \beta D^3 + \gamma D^5 + \ldots \qquad (3)$$

with $\alpha = 1/\epsilon_1$, where ϵ_1 is the permittivity at very small fields (i.e. zero bias). Such an equation is applicable to isotropic dielectrics, including ferroelectric materials at temperatures above the Curie point [9, 10], with strontium titanate possibly an extreme example since it behaves like a ferroelectric with a Curie point near 0°K [8].

If the fifth power and higher terms in equation 3 can be neglected, then, as shown by Roberts [9],

$$E \propto \left(\frac{\epsilon_1}{\epsilon} - 1\right)^{\frac{1}{2}} \left(\frac{\epsilon_1}{\epsilon} + 2\right) \qquad (4)$$

It can be seen from fig. 2b that the data are in good agreement with equation 4. Although a simple relationship for the permittivity in terms of the field cannot be obtained by rearranging equation 4 without some approximation, the following relationship was found to fit quite closely:

$$\frac{\epsilon_1}{\epsilon} + 1 = 2(aE^2 + 1)^{1/3} \qquad (5)$$

with

$$a = 4.1 \times 10^{-6}\,(\text{kV/cm})^{-2}$$

Various other equations of this type have been proposed for ferroelectric materials in the paraelectric state [11, 12].

Since the energy storage per unit volume is given by equation 1, substitution of $E = \alpha D + \beta D^3$ followed by integration gives

$$J = f(\epsilon)\,E^2$$

---

*Product of TAM Division, National Lead Company, New York.

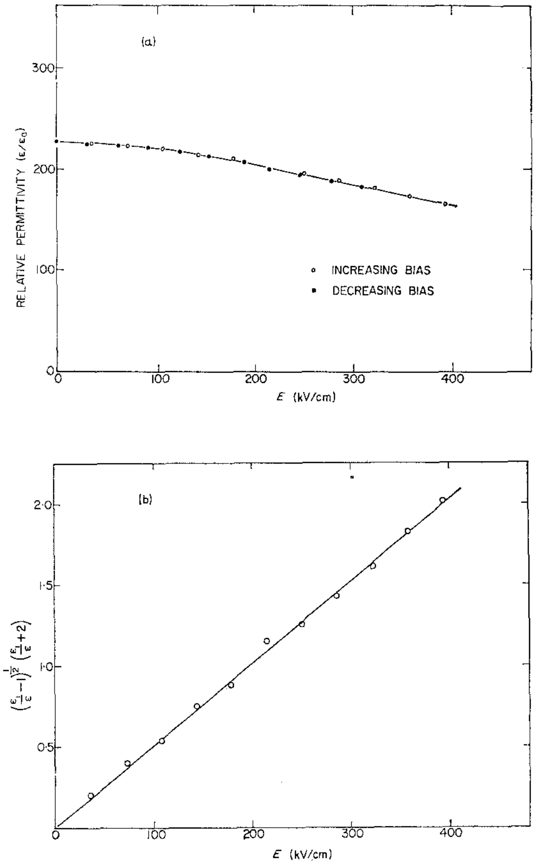

Figure 2 Influence of DC bias on the permittivity of the strontium titanate ceramic (ϵ_1 is the permittivity with zero bias).

where

$$f(\epsilon) = \tfrac{3}{4}\,\epsilon_1\left(\frac{\epsilon_1}{\epsilon}+2\right)^{-2}\left(\frac{\epsilon_1}{\epsilon}+5\right) \qquad (6)$$

Thus values of the stored energy could be obtained for a given field by obtaining the appropriate value of ϵ_1/ϵ either from fig. 2a or from equation 5. At 400 kV/cm, which was about the maximum breakdown strength of the capacitors, the calculated energy storage was 1.3 J/cm^3.

Although the material discussed here closely resembled ceramic strontium titanate in its properties, it is possible that a small amount of doping of the SrTiO$_3$ with barium from the glass might have taken place during firing, which together with the barium known to be present as impurity, might have resulted in a slight increase in permittivity and in non-linearity. However, no crystalline phase other than SrTiO$_3$ could be detected in the fired material by X-ray diffraction, and there was no evidence of a Curie point at temperatures down to − 200° C.

Because the relative permittivity of the strontium titanate ceramic had decreased only to 165 at 400 kV/cm (fig. 2a) it is unlikely that higher energy storage would be obtained by using a more linear material, for example calcium titanate ($\epsilon_1/\epsilon_0 \simeq$ 150 to 175), or TiO$_2$ ($\epsilon_1/\epsilon_0 \simeq 90$), unless appreciably higher fields were practical. Pennebaker [13] has reported breakdown strengths around 1500 kV/cm in strontium titanate films prepared by rf sputtering. At these fields the relative permittivity had decreased to approximately 90. Thus, even at 1500 kV/cm, energy storage in strontium titanate would probably be higher than in TiO$_2$.

3.2. Barium Titanate Ceramic

Small-signal permittivity measurements for the glass-bonded barium titanate ceramic are shown in fig. 3a. For fields below 200 kV/cm non-reversibility was evident and the measurements

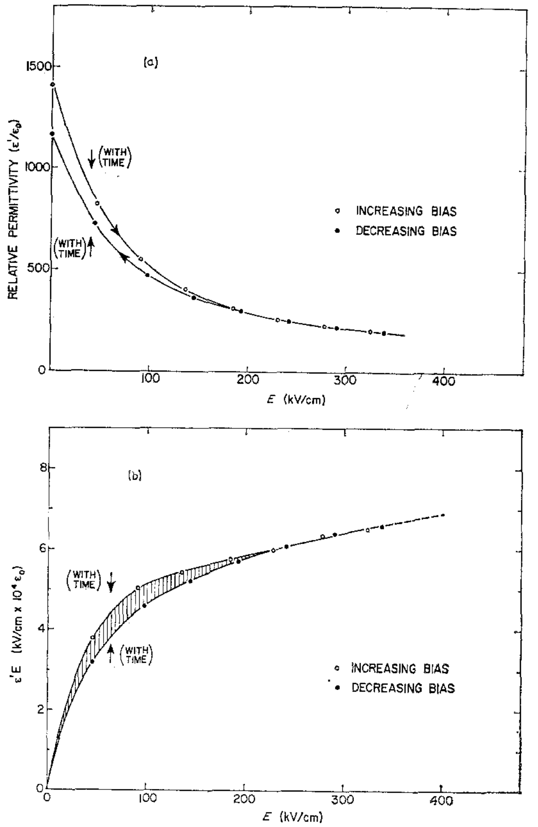

Figure 3 Influence of DC bias on the (small-signal) permittivity of the barium titanate ceramic.

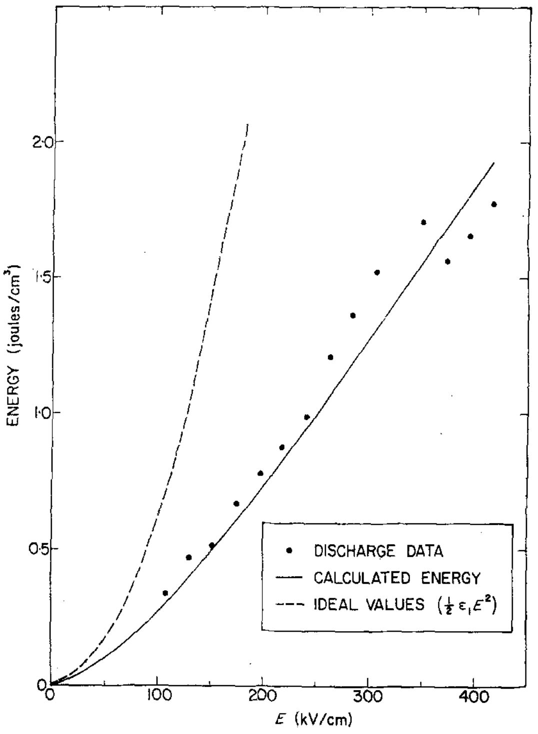

Figure 4 Energy storage in the barium titanate ceramic.

changed with time while the bias was being held constant. These effects are generally a consequence of domain reorientation in the material. Bearing in mind that the measured permittivity (ϵ') was probably slightly lower than the true differential value (ϵ) for fields less than 200 kV/cm, an estimate of the energy storage capability of the material at high fields was obtained by plotting $\epsilon' E$ against E (fig. 3b) and obtaining the integral in equation 2 graphically, using the data for decreasing fields. The shaded area in fig. 3b represents to some extent the energy absorbed by domain switching that is not recoverable on discharge.

Measurements made by the discharge method were found to agree quite closely with the predicted energy (fig. 4). The degree of departure from the ideal behaviour (constant capacitance) is also shown in fig. 4.

It is possible, of course, that higher energies might be obtained with other ceramic materials based on barium titanate [2], or on other ferroelectrics. Although high initial (zero bias) permittivity can be obtained by selecting a material with a Curie peak near room temperature, non-linearity is usually exaggerated in such cases as the Curie peak is generally shifted to higher temperatures by the application of the bias [10, 14]. Thus with a material of this type, the permittivity at high fields could be less than that of a material with lower zero-bias permittivity [14], and there might also be appreciable hysteresis losses [15]. However, as an alternative to the type of dielectric studied in the present work which has a combination of Curie peaks, a material such as a barium-strontium titanate [3] could be suitable if the Curie temperature were such that the permittivity maximum were shifted to the region of room temperature at high fields.

In fig. 5 energy storage in the barium titanate ceramic is compared with that in the strontium titanate ceramic, and with discharge data for glass-bonded lead zirconate [5]. In lead zirconate however, increased energy storage at lower fields can be obtained by using compositional additives that lower the threshold field needed to induce the ferroelectric phase. For example, for ceramics in the Pb (Zr, Ti, Sn) O_3 system [1, 4], a peak polarisation of 25 μC/cm^2 was reported to be typical at fields in the region of 40 to 50 kV/cm. Energy storage in this case was probably approaching 1 J/cm^3, and thus considerably higher than is likely to be obtained with other ceramic materials at these fields (fig. 5). With the glass-bonded lead zirconate, the benefit obtained by inducing the ferroelectric transition at high fields (cf fig. 1c) was offset to a large extent by the relatively low peak polarisation (approx. 9 μC/cm^2 [5]).

4. Conclusions

For fields up to 400 kV/cm the stored energy obtainable with ferroelectric or antiferroelectric ceramics is higher than for linear ceramics. Although the highest energy (2.1 $\pm$ 0.25 J/cm^3) was obtained with the antiferroelectric material this is likely to be the case only when the antiferroelectric-ferroelectric transition is induced at fields just below that chosen for the comparison. Ferroelectric ceramics with mixed Curie points and low remanence give high energy over a wide range of field strengths in spite of a large decrease in permittivity with increasing field.

In practice, the maximum energy density obtainable for a particular ceramic will generally decrease with increasing dielectric volume because breakdown strength will be reduced unless special efforts are made both to eliminate flaws in the dielectric (pores, microcracks, etc.)

[2, 3, 4], and to avoid field concentrations at electrode edges [3, 16].

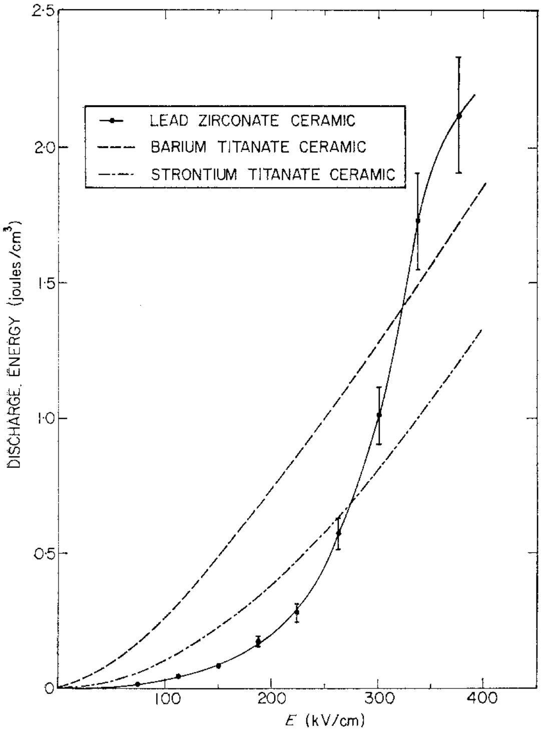

Figure 5 Comparison of the energy storage capabilities of the materials.

Acknowledgements

The writers are grateful to Dr G. H. Maher for advice on the construction of the thick-film capacitors, and to Dr F. H. Hielscher for assembling the equipment used for the pulse discharge measurements.

References

1. B. JAFFE, *Proc. IRE* **49** (1961) 1264.
2. G. J. HILL, *Proc. Brit. Ceram. Soc.* **18** (1970) 201.
3. P. H. KLEIN (Ed.) "High Energy Storage Ceramic Capacitor," (USAEC Report NYO-9076, 1960).
4. B. JAFFE "Research on Antiferroelectric Materials" (US Armed Services Tech. Inf. Agency Report AD 400, 331L, 1962).
5. I. BURN, *Bull. Amer. Ceram. Soc.* **50** (1971) 501.
6. G. H. MAHER, *Brit. Patent* 1,185,251 (1970).
7. C. HIRAYAMA, *J. Amer. Ceram. Soc.* **44** (1961) 602.
8. G. H. JONKER and J. H. VAN SANTEN, *Philips Tech. Rev.* **11** (1949) 183.
9. S. ROBERTS *Phys. Rev.* **71** (1947) 890.
10. A. F. DEVONSHIRE, *Adv. Phys.* **3** (1954) 85.
11. K. M. JOHNSON, *J. Appl. Phys.* **33** (1962) 2826.
12. G. RUPPRECHT, R. O. BELL and B. D. SILVERMAN, *Phys. Rev.* **123** (1961) 97.
13. W. B. PENNEBAKER, *IBM J. Res. Dev.* **13** (1969) 686.
14. H. DIAMOND, *J. Appl. Phys.* **32** (1961) 909.
15. V. V. KIRILLOV and V. A. ISUPOV, *Bull. Acad. Sci. USSR* (Phys. Ser.) **31** (1967) 1878.
16. T. I. PROKOPOWICZ, U.S. Patent 3,496,434 (1970).

Received 18 June and accepted 6 October 1971.