Optimization of energy storage density in ceramic capacitors

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Abstract. A theoretical treatment, based on the Devonshire theory of ferroelectrics, is presented to describe the storage of electrostatic energy in ferroelectric and paraelectric materials at very high field strengths. In all cases, optimal energy density is achieved by using compositions with Curie temperatures well below the operating temperature. The theory is applied to barium–strontium titanate ceramics and optimal compositions are deduced for energy storage at given working fields. The theory is supported by experimental data showing energy densities up to 8 J cm^{-3} at 100 kV mm^{-1}.

1. Introduction

Multi-layer capacitors with a dielectric consisting essentially of barium titanate ceramic are a common component in many electronic systems. Because of the extremely high dielectric constant of this material at room temperature, the capacitance per unit volume that can be achieved is very large and the units are also robust and cheap. It is found, however, that the effective capacitance decreases sharply as the applied voltage is increased, so that the energy storage density that can be achieved is disappointingly low.

It has long been recognized that this decrease in polarizability with electric field is an intrinsic property of ferroelectric ceramics and various approaches have been proposed to overcome the problem. Jaffe [1] suggested delaying the onset of the ferroelectric transition to higher fields by using a material that is antiferroelectric at the operating temperature but able to undergo a field-enforced transition to a ferroelectric state. This elegant solution does not appear to have resulted in practical devices yet. Burn and Smyth [2] examined the behaviour of barium titanate, strontium titanate and lead zirconate ceramics at fields up to 40 kV mm^{-1} and concluded that barium titanate can achieve a higher energy density (1.8 J cm^{-3}) than can strontium titanate (1.3 J cm^{-3}), but that lead zirconate, which is antiferroelectric and behaves in accord with Jaffe's suggestions, can achieve about 2.2 J cm^{-3} at this field. In a more recent report, Love [3] presented measurements on energy storage in a variety of ferroelectric and antiferroelectric materials with proprietary compositions, the most effective of which achieved an energy density of 6 J cm^{-3} at 90 kV mm^{-1}. The materials studied did not belong to a single family, but spanned

the field of possible compositions. Love concluded that 'surprisingly, maximum energy storage is not obtained in high dielectric constant materials but in those materials which display intermediate dielectric constant and highest ultimate breakdown voltage'.

It is the purpose of the present paper to present a rationale for the design of ferroelectric dielectrics to achieve maximum energy storage density, and to show that this allows the construction of capacitors with excellent energy storage capabilities. Our conclusion is even stronger than that expressed by Love. We conclude that, even for a fixed operating electric field strength, maximum energy storage density is achieved by adjusting the Curie temperature of the material so that it operates in the paraelectric domain and with a zero-field dielectric constant that is relatively small and in specified relation to the operating field strength.

We demonstrate these calculations and conclusions, and present confirmatory experimental results, for the case of barium–strontium titanate ceramics, although it may well be that other systems can achieve even higher energy densities.

2. Theory

In the analysis that follows we do not attempt to set up a rigorous or sophisticated theoretical analysis, since the material parameters are insufficiently well known for this to be useful, even were it feasible. We are content, rather, to develop a theory that is better than semiquantitative and that serves to guide the experiments.

2.1. Theory of ferroelectrics

The general behaviour of ferroelectrics in single-crystal form is well described by the theory developed by Devonshire [4, 5]. We outline this theory in a form suitable

for our subsequent calculations. In the single-crystal case we are interested in the equilibrium polarization of a crystal under the influence of an electric field and under conditions of zero external stress. If we deal with systems of the perovskite family, which includes barium titanate and strontium titanate, then the high-temperature paraelectric phase is cubic. We can therefore write the free energy of the system, per unit volume, in an electric field (E_x, E_y, E_z) in the form

$$
\begin{aligned}
G = G_0 &+ a(P_x^2 + P_y^2 + P_z^2) + b(P_x^4 + P_y^4 + P_z^4) \\
&+ c(P_x^6 + P_y^6 + P_z^6) + d(P_y^2 P_z^2 + P_z^2 P_x^2 + P_x^2 P_y^2) \\
&+ e(P_y^2 P_z^4 + P_z^2 P_y^4 + P_z^2 P_x^4 + P_x^2 P_z^4 + P_x^2 P_y^4 + P_y^2 P_x^4) \\
&+ f P_x^2 P_y^2 P_z^2 + \cdots - (E_x P_x + E_y P_y + E_z P_z)
\end{aligned}
\tag{1}
$$

where P_x, P_y and P_z are the polarizations along the three $\langle 100 \rangle$ cube axis directions, a to f are constants and G_0 represents all the other terms in the free energy. The expansion in terms of polarization has been truncated arbitrarily at sixth-order terms, and is therefore not exact. The Devonshire theory for the case of barium titanate [4] is actually based upon a reduced version of this expression with e and f set arbitrarily equal to zero in order to reduce the number of parameters. The more generally presented form of the theory [5] is a one-dimensional version with $P_x = P_y = 0$ and only $P_z \neq 0$ further reducing the number of parameters.

As is well known from the Devonshire theory, we proceed by assuming a linear temperature variation for the first coefficient

$$
a = a_0(T - T_0) \tag{2}
$$

and take a_0 and all the other coefficients $b, \ldots, f$ to be independent of temperature. This leads to a behaviour for the dielectric constant ϵ parallel to a cube axis in the high-temperature paraelectric regime given by the Curie–Weiss law

$$
\epsilon = \frac{1}{\epsilon_0} \left(\frac{\partial P}{\partial E} \right)_{E \to 0} = \frac{(2a_0 \epsilon_0)^{-1}}{T - T_0} = \frac{C}{T - T_0} \tag{3}
$$

and a transition to a tetragonal ferroelectric state ($P_x = P_y = 0$, $P_z \neq 0$) below a Curie temperature T_C given by

$$
T_C = T_0 + \frac{b^2}{4a_0 c}. \tag{4}
$$

If $b < 0$ the phase transition is of first order; if $b > 0$ it is of second order. The coefficients of the terms of highest order, c, e and f, are necessarily positive if the crystal structure is to be stable. The spontaneous polarization for $T < T_C$ is temperature dependent, and extrapolates to a limiting value

$$
P_S = \frac{-b + [b^2 - 3a_0 c(T - T_0)]^{1/2}}{3c} \tag{5}
$$

as $T \to 0$, provided that we do not encounter further phase changes. The expressions (3)–(5) can be inverted to give the parameters a, b and c of the model in terms of the measured quantities C, T_C and P_S. This is the normal one-dimensional form of the theory [5].

In the case of barium titanate, the full three-dimensional expression (1) is required to represent completely the observed behaviour. As the crystal is cooled, the first transition is to a ferroelectric state with polarization along one of the cube axes, giving a tetragonal structure, as represented in the simple model above. As the temperature is further lowered there are two more transitions, first to a monoclinic state with polarization along a [110] direction and then to a rhombohedral state with polarization along [111]. Information about the location of these three Curie temperatures, together with other available experimental data, is sufficient to determine all seven parameters in the free energy function G of (1), within the accuracy of the model. First we impose the symmetry of the phase in question: $P_x = P_y = P_z = 0$ for the high-temperature paraelectric phase, $P_x = P_y = 0$ for ferroelectric phase 1, $P_x = P_y$, $P_z = 0$ for phase 2 and $P_x = P_y = P_z$ for phase 3. We then find the equilibrium polarization for the phase in question by setting $\partial G / \partial P = 0$ and evaluate its free energy function by substituting this expression in (1). The equilibrium phase at any temperature is that having lowest free energy, so that knowledge of the three Curie temperatures provides three relations between the coefficients. Two further relations come from knowledge of the Curie constant and Weiss temperature in the paraelectric region, a further one from the spontaneous polarization in phase 1 and a seventh relation from the relation between the longitudinal and transverse dielectric constants in ferroelectric phase 1.

It is possible to estimate the coefficients $a_0, b, \ldots, f$ for pure barium titanate from the published single-crystal data, provided that we make the assumption that they are all independent of temperature. The actual values, and even the signs, depend upon the number of coefficients included, however, so that there are considerable discrepancies between the common members of a full set and of the more limited set evaluated by Devonshire. Ideally we should like to have enough experimental data to evaluate these coefficients to a reasonably high order for all materials to be included in our treatment. In practice, as we see presently, data limitations restrict what is possible.

2.2. Energy storage density

It is now a straightforward matter to calculate, from (1), the energy stored in the polarized ferroelectric material. If we apply an electric field in an arbitrary direction, then minimization of the free energy requires that $\partial G / \partial P_x = 0$, $\partial G / \partial P_y = 0$ and $\partial G / \partial P_z = 0$. These three equations determine P_x, P_y and P_z and thus, by integration from zero field, the stored energy density U given by

$$
U = \int_0^E \boldsymbol{E} \, d\boldsymbol{P} = \varepsilon_0 \int_0^E E \varepsilon(E) \, dE \tag{6}
$$

where $\varepsilon(E)$ is the small-signal dielectric constant at field E and ε_0 is the permittivity of free space. Vector quantities are used in the first form of writing because the polarization is not generally parallel to the applied electric field.

For a detailed treatment in the ferroelectric domain below T_C we should really take into account the hysteresis

of polarization flipping. This can be calculated for an infinite crystal with no domain walls or for a particular crystal model with specified domain-wall resistance. We are really interested in the available energy on discharge, however, which is represented formally by (6) with the limits of integration reversed and a minus sign inserted. This result is rather simpler, since the crystal remains in its equilibrium polarized state when the field is removed, and is given by (6) if $P(E)$ is taken to have its equilibrium value. In practice we shall actually be concerned only with the paraelectric domain in our calculations, so that the apparent complication does not arise.

2.3. The isotropic approximation

Calculation of the stored energy is simplest if we choose a high-symmetry direction in the crystal, so that P is parallel to E. The calculated variation of stored energy with orientation depends upon the terms retained in the free energy expansion (1) and the values assigned to the coefficients d, e and f. In the case of pure barium titanate, the full set of coefficients deduced from experimental data suggests an anisotropy in stored energy density in the paraelectric region amounting to about 30%, but there does not appear ever to have been an experimental investigation of this point. In the case of strontium titanate and the strontium–barium mixed titanates that we wish to discuss here, there is not enough information to allow us to evaluate the higher coefficients. It therefore appears best to use an isotropic approximation for these materials. Although this is not justified in the ferroelectric region below the Curie temperature, our concern will be almost exclusively with the paraelectric region $T > T_C$.

Formally an isotropic approximation involves the assumptions

$$d = 2c \qquad e = 3c \qquad f = c \qquad (7)$$

which are fulfilled only approximately for pure barium titanate. On the basis of (7) we can write the free energy expression (1) in the form

$$G = G_0 + aP^2 + bP^4 + cP^6 - EP \qquad (8)$$

where P and E are simply the magnitudes of the polarization and electric field vectors. The expression (8) is just that used in the simplest form of the Devonshire theory. Although we need to take account of anisotropy within the ferroelectric region, we shall use the simple isotropic expression within the paraelectric region that is our prime interest.

3. Application to ceramics

We are concerned here with optimizing the energy storage properties of practical capacitors with a multi-layer ceramic structure. The basis of the strategy that we propose is to vary the Curie temperature of the material by appropriate chemical additions, taking account of unavoidably related changes in other material properties. For practical reasons

it is sensible to start from the well-developed technology of capacitors based upon barium titanate.

Experimental results summarized by Jaffe *et al* [6] show that the Curie temperature of barium titanate can be lowered by progressive replacement of barium by strontium or of titanium by zirconium, hafnium or tin. Conversely it can be raised by addition of lead, but this is not the direction in which we want to proceed. In all cases the two end members of the series are completely miscible, so that substitution can proceed to the 100% level. These substitutions do not alter the three transition temperatures of the material in the same way, however, and a detailed theoretical treatment would need to take account of this by progressive change in the relative magnitudes of the coefficients of the model (1). There are insufficient data available to make this connection at the present time, so that we use the simpler model (8) as discussed above. This is not a large sacrifice since it will become apparent that energy storage density is optimized by operation in the paraelectric range.

A practically convenient system with which to work is the mixed titanate $Sr_xBa_{1-x}TiO_3$, because the technology of making multi-layer ceramic capacitors based on these materials is well established. Barium and strontium titanates both have the cubic perovskite structure in the paraelectric state and are mutually soluble, so that the parameter x can be varied between 0 and 1. The Curie temperature of strontium titanate is also very close to 0 K, so that the whole Curie temperature range between 0 and 420 K is accessible.

The particular readily measurable parameters are the Curie temperature T_C, the Weiss temperature T_0, the Curie constant C and the spontaneous polarization as a function of temperature, but particularly its value P_S extrapolated to 0 K. Because we intend to work with ceramics rather than single crystals, it is desirable to measure these physical quantities on appropriately fired ceramic sheets with approximately the final design grain-size distribution. The dielectric properties of $BaTiO_3$ are, in fact, known to be influenced appreciably by grain size in the case of extremely fine-grained ceramics [7], but the grain sizes used in our application are typically greater than 1 μm and the effects are not significant.

The variations of T_C, T_0 and C with the composition parameter x can all be found from measurements of the low-field dielectric constant over an appropriately large temperature range, encompassing the paraelectric region and the upper part of the first ferroelectric region. The saturation polarization P_S can similarly be evaluated by examination of the high-field hysteresis loop over a temperature range extending down to about 4 K. Evaluation of the temperatures T_C and T_0 presents no problems of interpretation, but further discussion is needed in the cases of C and P_S.

The ceramic material with which we deal is formed by sintering a fine powder, in which the crystallites are nearly isometric in form. The crystallite orientations in the unfired ceramic precursor are random, and these orientations are locked in by the sintering process, which achieves better than 97% of the ideal density. The

sintering temperature is typically 1200–1300 °C, and thus well above the Curie temperature, so that all cube axes in the crystallites are equivalent. On cooling below the ferroelectric transition temperature T_C, the crystallites tend to assume a tetragonal ferroelectric form. Because this involves lattice distortions, however, the polarization c axes are constrained to be distributed statistically at random. There are other complications caused by piezoelectric effects, which have been omitted from the free energy function (1) but have been considered by Shaikh *et al* [7]. The main effect of the elastic strains is to broaden the ferroelectric transition and, apart from the difficulties this imposes on the measurement of T_C need not concern us here.

When a small electric field is applied to the ceramic in its unpolarized paraelectric state, the dielectric response essentially measures the reciprocal of the quantity $a_0(T - T_0)$, as given by (3). Because $P_x^2 + P_y^2 + P_z^2 = P^2$, the dielectric constant is independent of field orientation. Measurement over a temperature range thus yields both T_0 and C, which is proportional to a_0^{-1}, in the same way as in a single crystal.

In the tetragonal ferroelectric domain, however, application of an electric field can only cause reversal of polarization, any 90° reorientations being inhibited by elastic strain constraints. In the saturated state, therefore, the measured spontaneous polarization P_S' when the field is removed is

$$P_S' = \int_0^{\pi/2} P_S \cos\theta \sin\theta \, d\theta = \tfrac{1}{2} P_S. \qquad (9)$$

We can therefore, in principle, evaluate the single-crystal value P_S very simply from the measurements. This conclusion requires some additional comment, however, since the experimental value is presumably that applying to whatever is the low-temperature structure, rather than being a simple extrapolation of that for the tetragonal structure that is stable just below the Curie temperature. For ceramics, however, the measured value extrapolates smoothly to low temperatures and saturates once the temperature is appreciably less than T_C. We take this value to be the saturation polarization P_S used in relation (5).

3.1. Material properties

There are some reported measurements of the properties of mixed strontium–barium titanates in the literature [8–10], but these are not extensive enough to allow reliable estimation of the variations of the relevant model parameters with composition. We have therefore carried out a series of measurements on the whole range of compositions of these materials in ceramic form, and the results are reported in a companion paper [11] in which full details are given. The single-crystal spontaneous polarization P_S deduced from the measurements is taken as being twice the ceramic value P_S', whereas the measured Curie constant C is taken to be equal to the single-crystal value, as discussed above. Within the range of overlap the measured results are in reasonable agreement with those reported elsewhere in the literature. The behaviour of
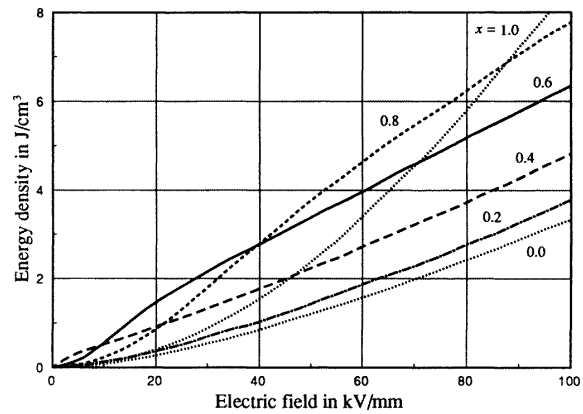

Figure 1. Calculated energy storage density for $Ba_{1-x}Sr_xTiO_3$ ceramic material as a function of working electric field, and with the composition variable x as a parameter. The parameters of the model have been assumed to vary in accord with equations (7) and (8) as discussed in the text.

these measured quantities over the whole composition range $0 \le x \le 1$ can be expressed, to moderate accuracy, by the equations

$$T_C \approx 400 - 220x - 160x^2$$

$$T_C - T_0 \approx 10(1 - x)$$

$$C \approx 1.2 \times 10^5 (1 - 0.5x^2) \qquad (10)$$

$$P_S = 2P_S' \approx 0.36(1 - 0.5x).$$

As discussed above, we necessarily base our analysis on an isotropic model with the coefficients d, e and f in (1) set equal to zero and calculate a_0, b and c from the experimental data by inverting equations (3)–(5). This is most easily done numerically, for different values of the composition parameter x during the course of the calculations.

3.2. Energy storage density

Although the approach that we have developed is quite general, we apply it specifically to the barium–strontium mixed titanates, for which the data on variation of physical parameters with composition were given in the previous section. The results are shown in figure 1, in which we plot calculated energy storage density as a function of working field strength for the whole range of the composition parameter x. The assumed working temperature is taken as 300 K, which is near room temperature.

The curves in figure 1 exhibit several interesting features. Most of the curves are S-shaped, when viewed on an appropriate scale, except that for pure strontium titanate which is a simple parabola, reflecting the linear dielectric behaviour when $T_0 = T_C$ as approximated by the experimental results (10). Such completely linear behaviour is, however, not realistic, and arises from the fact that we have neglected all terms of order higher than the sixth in the free energy expansion. At any given working field there is an optimal composition for the ceramic material, the mole fraction of strontium increasing with increasing
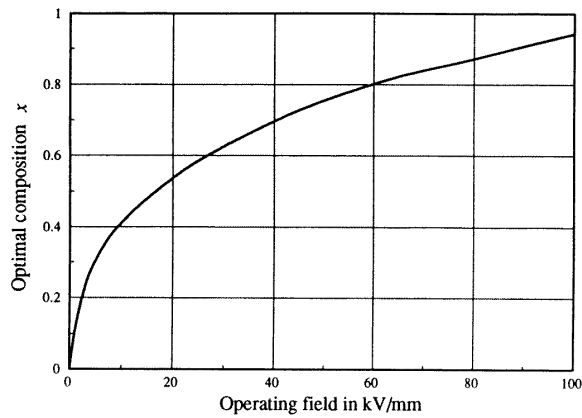
Figure 2. Calculated optimal composition parameter x for $Ba_{1-x}Sr_xTiO_3$ ceramic material as a function of working field.

field strength. The envelope of these curves, giving the maximum attainable energy density for this family of materials, is approximately linear over the electric field range shown and has the form

$$U_{\max} \approx 0.08E \qquad (11)$$

when SI units are used. A high working field is clearly desirable, and 100 kV mm^{-1} is probably about the maximum that can be reliably attained. In the range 50–100 kV mm^{-1}, the optimal composition is in the range about 70–90% strontium titanate, as shown in figure 2.

In the units more commonly used in this field, and taking account of the slightly superlinear behaviour to which (11) is an approximation, an energy density of about 4 J cm^{-3} should be attainable with this ceramic system at the usual breakdown field of about 50 kV mm^{-1}. If the breakdown field can be increased to 100 kV mm^{-1}, then an energy density of about 8 J cm^{-3} becomes attainable.

3.3. Extensions of the analysis

The theory developed above applies to a ferroelectric material over the whole temperature range, both below and above its Curie temperature. The predicted energy-storage capacity of materials at temperatures below their Curie temperature is relatively low, since most of the polarization develops at very low fields. The theory, being an equilibrium rather than a dynamic one, does not take account of hysteresis in the polarization behaviour and domain wall motion, and so gives a somewhat low prediction for energy storage in materials below the Curie temperature, but this does not significantly modify the predicted energy density at high fields. It is straightforward, but hardly worthwhile, to extend the theory to include such hysteresis effects.

The theory has been applied here explicitly only to the case of first-order ferroelectric materials, for which there is a discontinuity in polarization at the Curie temperature. This is represented in the theory by the assumption that $b < 0$ and $c > 0$. The alternative assumption that $b > 0$ and $c \geq 0$ provides a description of the behaviour

of a second-order ferroelectric, in which there is no discontinuity in polarization at the Curie temperature, the spontaneous polarization simply rising sharply from zero as the temperature is lowered below T_C. The energy-storage behaviour is very similar in the two cases, with absolute values depending upon the magnitude of the physical quantities P_S and C. There appears to be no particular advantage or disadvantage associated with the nature of the ferroelectric phase transition.

We have illustrated here the quantitative application of the theory only to the ceramic system $Ba_{1-x}Sr_xTiO_3$. Similar analysis applies, however, to other candidate systems. On the basis of the general form of the theory, it is apparent that the value of the spontaneous polarization P_S, the Curie temperature T_C and the breakdown field E_B are the three parameters of prime importance. The way in which these parameters vary with composition is significantly different from one ferroelectric system to another, so that the search for an optimal dielectric composition is by no means exhausted by the examination of the barium–strontium titanate ceramics considered here.

4. Experimental results

As a check on the basic correctness of the theoretical treatment, measurements were made on $Ba_{1-x}Sr_xTiO_3$ ceramics with a composition range from $x = 0$ to $x = 1$. Details of these measurements and of the results are the subject of another paper [11]. The samples with $x = 0.2$ and 0.3 were made from commercially available pre-mixed powders prepared by a hydrothermal method, and the remainder from powders that we prepared by calcining strontium–barium titanyl oxalate mixtures at temperatures in the range 750–900 °C. The powders were mixed with binding agents and either pressed directly into a mould or made as a slurry and cast into thin (20–50 μm) green sheets by the doctor-blade technique. The specimens were heated to remove the binders and then sintered at temperatures in the range 1200–1400 °C. SEM micrographs of the specimens gave estimated porosities in the range 2–3%. Electrodes were either printed onto the green tape or painted onto the bulk specimens. These specimens were used to determine material properties as described in the companion paper [11].

Stored energy was determined by measuring sample capacitance with a small 1000 Hz AC signal while superimposing an increasing DC bias and then integrating the result. As a check of correctness, some additional measurements were made by charging and discharging the sample capacitance through a calibrated resistor, monitored with an oscilloscope, and integrating the resulting curve. These measurements were mostly made at room temperature, though a few were carried out at higher temperatures to verify the predictions of the theory. In all cases, measurements were continued until either the breakdown voltage of the specimen or the voltage capability of the measuring equipment was reached. The experimental results are shown in figure 3.

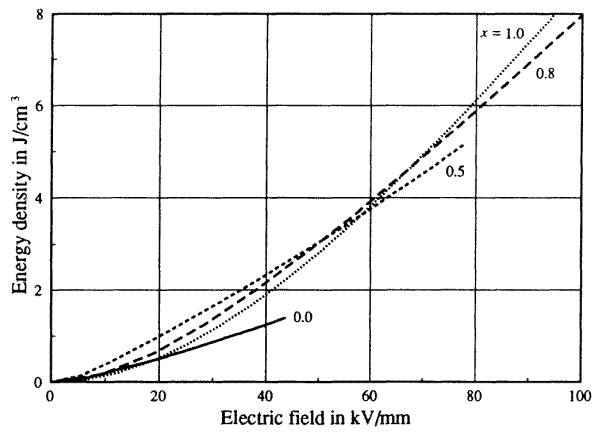It can immediately be seen that the general predictions of the theory are well supported. Energy storage density

Figure 3. Measured energy storage density for $Ba_{1-x}Sr_xTiO_3$ ceramic material as a function of working electric field and with the composition variable x as a parameter.

is indeed maximized at a particular working field by use of an appropriate value of the composition variable x, and the optimal value of x increases as the working field is increased. At the highest working field attainable in our measurements, 100 kV mm^{-1}, the optimal composition has $x \approx 1$ implying pure strontium titanate, in good agreement with theoretical predictions. At more usual working fields around 60 kV mm^{-1}, the optimal composition has $x \approx 0.8$. The attainable energy density over the whole range of composition and field strength shows quite good agreement between theory and experiment.

In view of the experimental uncertainty in some of the material constants and the very simple nature of the theory, this degree of agreement is very gratifying, particularly since the experimental values also suffer from some uncertainty. A formally improved theory could have been constructed by including more high-order terms, but the basic Devonshire theory is itself highly simplified, and we should not expect it to give more than a moderately accurate prediction of the behaviour of real materials in any case.

5. Conclusions

We have developed here a set of design principles for high-energy-density capacitors using ferroelectric ceramic material as the storage medium. If the material properties are known, then the theory allows us to optimize the energy density. Realization of these design principles for the case of mixed strontium–barium titanate material verifies their essential correctness. Using this approach, material with energy density of approximately 8 J cm^{-3} at 100 kV mm^{-1} has been successfully produced and tested. The theory is applicable to a search for even higher energy densities and work along these lines is proceeding.

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