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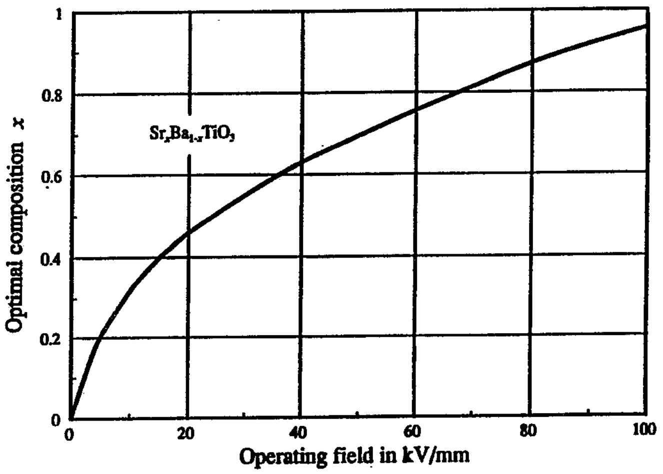

(57) Abstract

Multilayer capacitors comprise layers of a dielectric material interleaved with metallic electrodes. To improve the energy storage of such capacitors when operating in field strengths greater than 20 kV/mm, the dielectric material is a modified ceramic material comprising a base material and an additive. The base material is a ferroelectric ceramic material having (i) its ferroelectric Curie temperature either greater than or lower than the working temperature of the capacitor, (ii) a large value of spontaneous polarisation near 0 °K and (iii) a large Curie constant. The additive forms mixed crystals with the base material without significantly changing its crystal structure, spontaneous polarisation or Curie constant, but reduces its ferroelectric Curie temperature to a value at least 50 °C below the capacitor working temperature. If the base material is barium titanate, the preferred additive is at least 40 atomic per cent strontium titanate.

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TITLE: "CERAMIC DIELECTRIC MATERIALS FOR HIGH ENERGY STORAGE CAPACITORS"

Technical Field

This invention concerns ceramic dielectric materials. More particularly, it concerns dielectric materials which, when used in multi-layer capacitors, enable improved energy storage density to be achieved with such capacitors.

Background to the Invention

Multi-layer capacitors constructed using a ceramic dielectric material have been known for some time. These capacitors commonly have layers of dielectric material, each layer being about 20 micrometres thick, interleaved with metallic electrodes. Several tens of layers are used to make a typical capacitor, but many more layers can be combined to make a large capacitor.

The dielectric material commonly used in such capacitors is barium titanate, with small additions of strontium titanate, manganese, and/or other materials. These additives reduce the variation of capacitance with temperature and improve the breakdown behaviour of the capacitors. Barium titanate is a ferroelectric material at room temperature and can have a dielectric constant as large as 40,000 near its Curie temperature of 140°C. (The Curie temperature, T_c, is the temperature above which the material ceases to be a ferroelectric material and becomes a paraelectric material.) However, the dielectric constant of barium titanate varies greatly with temperature, which is a significant disadvantage. Hence it has become common practice to add up to 20 per cent strontium titanate to the barium titanate, which reduces the Curie temperature so that it is around room temperature. The addition of the strontium titanate is usually effected in a manner such that the resultant ceramic dielectric material has an inhomogeneous composition, and thus there is effectively a spread of Curie temperatures of the mixed ceramic.

Most multi-layer capacitors are used at low electric field strengths. As the voltage applied to a capacitor is increased, the dielectric constant of the ceramic materials decreases rapidly, with the result that the stored energy density of the capacitor is not high. As noted by I Burn and D M Smyth in their paper entitled "Dielectric Storage in Ceramic Dielectrics", which was published in **Journal of Materials Science**, Volume 7, 1972, pages 339 to 343, the maximum energy storage in capacitors made with barium titanate and strontium titanate dielectric materials is around 2.0 joules per cm^3 for fields up to about 40 kV/mm. Typical energy storage at fields of 40 to 50 kV/mm is quoted in that paper as being around 1 joule per cm^3 when ceramic dielectric materials of the $Pb(Zr,Ti,Sn)O_3$ system are used.

Since most uses of multi-layer capacitors require the capacitors to work at low field strengths, the capacitors currently available commercially have met most needs, and an electrolytic capacitor is used when the capacitor needs to function in higher electric fields, and when a high energy storage is required.

Two examples of such high electric field strength uses of capacitors are (i) heart pacemakers with defibrillation features and (ii) camera flashes. At present there is no suitable small multi-layer capacitor for heart pacemakers with defibrillator circuitry. Thus relatively large electrolytic capacitors are used in such implants. The energy storage capacity of the electrolytic capacitors is around 2 to 3 joules per cm^3. Clearly, it would be advantageous to avoid the size penalty in heart pacemakers, and in camera flashes and other electronic circuitry requiring higher energy storage, by providing capacitors having a smaller volume and a higher energy storage density than is currently available for such capacitors.

Disclosure of the Present Invention

It is an objective of the present invention to provide ceramic dielectric materials for use in multi-layer capacitors which enable the energy storage density of such capacitors to be significantly increased when the capacitors are used in field strengths of from 20 kV/mm to about 100 kV/mm.

This objective is achieved by modifying a ferroelectric ceramic material to bring its Curie temperature to a value well below the working temperature of the capacitor.

Now the behaviour of a ferroelectric material is substantially defined by (i) the temperature below which its state changes from paraelectric to ferroelectric (the Curie temperature, T_c, as noted above), (ii) the Curie constant C which describes its dielectric behaviour at temperatures above T_c, and (iii) its spontaneous polarisation P_s in its ferroelectric state, extrapolated to absolute zero temperature. The ferroelectric materials which are suitable for modification in accordance with the present invention are those with high values of C and P_s. The behaviour of these ferroelectric materials is modified by the addition of a material which has a crystal structure compatible with that of the ferroelectric material, in such concentrations that the Curie temperature of the ferroelectric material is lowered to a value which is at least 50°C below the desired operating temperature of the completed capacitor (and preferably at least 100°C below that operating temperature), while neither the Curie constant nor the spontaneous polarisation is substantially reduced. The resulting ceramic dielectric material, therefore, operates in its paraelectric range. It is also important that the resulting material will have a high electrical breakdown strength.

Ferroelectric materials suitable for modification in accordance with this invention include those which have the perovskite crystal structure, and which undergo a displacive ferroelectric transition at the Curie temperature that is associated with the frequency of an optical mode phonon at the centre of the Brillouin zone tending to zero. Materials of this class include the titanates of elements from the second column of the periodic table, such as barium titanate, as well as certain niobates, zirconates and tantalates.

A particularly useful realisation of the present invention comprises barium titanate, modified by the addition of strontium titanate. This modified material is, in fact, a mixed strontium/barium titanate material, having the formula $Sr_xBa_{1-x}TiO_3$, with the strontium titanate comprising more than 40 mole per cent of the mixture. Preferably the strontium titanate comprises from 50 to 95 mole per cent of the mixture, and more preferably from 70 to 90 mole per cent of the mixed titanate.

Thus, according to the broadest form of the present invention, there is provided a modified ceramic material suitable for use as a dielectric material in multi-layer capacitors, said modified ceramic material comprising a base material having a displacement ferroelectric transition (such as that exhibited by ferroelectric materials having the perovskite crystal structure) and an additive distributed therein, characterised in that

(a) the base material is a ferroelectric ceramic material having (i) a ferroelectric Curie temperature which is either higher or lower than the temperature at which said capacitors are to be used (the working temperature), (ii) a large value of spontaneous polarisation below its Curie temperature, and (iii) a large value of the Curie constant;

(b) the additive is a material which (i) forms mixed crystals with the base material without changing its crystal structure, (ii) does not significantly decrease the spontaneous polarisation or the Curie constant of the base material, and (iii) reduces the Curie temperature of the base material;

(c) the additive is distributed substantially uniformly within the base material; and

(d) the amount of additive present in the modified ceramic material reduces the Curie temperature of the base material to a value at least 50°C below the working temperature.

The present invention also encompasses (i) a method of making thin layers of such modified ceramic materials, and (ii) multi-layer capacitors which include the modified ceramic material of the present invention as the dielectric material of the capacitor.

The significance of the various features of the present invention will become more apparent from the following discussion of the theoretical explanation of the present invention and the subsequent description of embodiments of the invention. In the following discussion and description, reference will be made to the accompanying drawings.

Brief Description of the Drawings

Figure 1 is a graph showing the variation of energy density with applied electric field for a series of strontium/barium titanate materials having differing strontium titanate concentrations, as calculated using the theoretical model developed by the present inventors.

Figure 2 is a graphical depiction of the way in which the strontium titanate component of mixed strontium/barium titanates should be chosen, for optimal energy storage density, according to the operating field in which capacitors having the mixed titanates as their dielectric materials are to be used.

Figure 3 shows (again, in graph form) the measured stored energy density of some strontium/barium titanates, as a function of the field strength applied to the material.

The Theory of Ferroelectrics

The general behaviour of single crystals of ferroelectric materials is well described by the theory which is usually credited to A F Devonshire, and which is set out in his papers entitled "Theory of Barium Titanate" (published in **Philosophical Magazine**, volume 40, 1949, pages 1040 to 1063, and volume 42, 1951, pages 1065 to 1079) and "Theory of Ferroelectrics" (published in **Advances in Physics**, volume 3, 1954, pages 85 to 130). This theory is based upon a consideration of equilibrium polarisation of a crystal under the influence of an electric field and under conditions of zero external stress. The theory successfully describes the behaviour of crystals having the perovskite structure (which includes barium titanate and strontium titanate, and also other materials in which the frequency of an optical mode phonon at the centre of the Brillouin zone tends to zero), including the observed change of state or phase of the crystals, from a paraelectric state above a transition temperature known as the Curie temperature, T_c, to a ferroelectric state below the Curie temperature. The theory, when extended to include terms in the sixth power of the polarisation P, also accounts satisfactorily for the existence and properties of the two other ferroelectric phases that occur at temperatures below that at which the normal tetragonal ferroelectric phase is thermodynamically stable. The theory also defines

(a) a "Weiss temperature", T_o, which is incorporated in the coefficient of the P^2 term in the free energy equation of the crystal (P being the polarisation of the crystal);

(b) a "Curie constant", C, which is defined by a relationship for the dielectric constant when the material is in the paraelectric phase; and

(c) the spontaneous polarisation extrapolated to 0°K, P_s.

The Curie temperature, the Weiss temperature, the Curie constant and the spontaneous polarisation extrapolated to 0°K are readily measurable (the last parameter being deduced from observations of the high-field hysteresis loop over a temperature range extending down to about 4°K). Direct measurements have now shown the way in which these important material parameters depend on the material composition produced by the addition of strontium titanate and certain other materials to barium titanate.

The theory is known to provide a reasonably good account of the ferroelectric behaviour of pure barium titanate in the form of single crystals. The present inventors have extended this theory to cover the case of an electric field applied at an arbitrary angle to the crystallographic axes, and thus to the behaviour of a ceramic consisting of a randomly oriented, densely packed mass of small crystals. The extension of the theory developed by the present inventors describes, to a similar approximation, the behaviour of barium-strontium titanate ceramics and other mixtures.

Using the behaviour of the Curie temperature $\mathbf{T_c}$, the Weiss temperature $\mathbf{T_o}$, the Curie constant **C** and the spontaneous polarisation $\mathbf{P_s}$ appropriate for a particular strontium-barium mixed titanate, the present inventors have calculated the stored energy density **U** in an applied working electric field $\mathbf{E_w}$ from the relationship

$$U = \int_{o}^{E_w} E.dP$$

where **P** is the dielectric polarisation under the applied electric field **E**. Repetition of this calculation for a wide range of material compositions and working fields produced the set of curves shown in Figure 1. Clearly, for any given working field, there is a particular concentration of strontium titanate in a barium-strontium titanate mixture which maximises the stored energy.

Figure 2 shows the optimal strontium concentration as a function of the working field for such a mixed strontium/barium titanates. In a typical low field use of multi-layer capacitors using such ceramic materials as dielectrics, the field will be less than 1.0 kV/mm. However, in pacemakers and in camera flashes and the like, the capacitors will be required to operate in fields of from 30 to about 100 kV/mm at room temperature. It will be seen from Figure 2 that the strontium titanate concentration of the mixed ceramic should be at least 40 mole per cent, and if the dielectric is to be used in capacitors which will be operated in higher fields, the strontium titanate concentration should be in the range of from 50 mole per cent to about 90 mole per cent, as calculated from this extension of the theory.

Embodiments of the Present Invention

To test the validity of the present inventors' extension of the theory of ferroelectrics, the inventors have made samples of mixed strontium/barium titanates by sintering powders having predetermined concentrations of strontium titanate and barium titanate. These powders were prepared by making solutions of an appropriate mixture of barium and strontium salts, and precipitating mixed salt crystals. The precipitated crystals were ground to ensure a uniform small particle size of the resultant powder. A slurry was made of this powder and a conventional organic binder. The slurry was cast onto a moving belt, and a doctor blade was used to form thin strips or tapes of the cast material on the belt. The tapes of "green" ceramic material thus formed had electrodes painted or printed on them, after which they were formed into stacks. The stacks were laminated under pressure, and were heated to a temperature sufficient to burn out the binder before being sintered at high temperature. The doctor blade casting of the "green" tapes effectively packed the titanate crystal orientations randomly in the green ceramic. The sintering process, by which better than 98 per cent of the ideal density was achieved, locked in the random crystal orientations.

Metal electrodes were applied to the laminated and sintered stacks of ceramic tapes thus produced to create individual multi-layer capacitors. The stored energy of these capacitors was measured at various applied voltages. From the sample dimensions, the stored energy density at each applied voltage was calculated. Figure 3 is a plot of the measured stored energy density as a function of applied electric field strength, for samples with a wide range of strontium concentrations.

It will be seen from Figure 3 that, for the particular example of a working electric field of 80 kV/mm, the optimal energy storage is achieved for a strontium titanate concentration of about 80 per cent, and that the stored energy density for that material is about 6.5 joules/cm^3 - a significant improvement on prior art materials. These and other experimental data have shown very good agreement with the theoretical predictions. Indeed, some results indicate a performance (in terms of stored energy density) some 20 per cent better than that predicted. This result is within the predictive accuracy expected of the extended theory and the discrepancy is not significant.

It is acknowledged that some dielectric properties are influenced by factors not discussed above. For example, the dielectric properties of barium titanate are known to vary appreciably with grain size when this ceramic is very fine-grained (that is, when its grains have a diameter less than 0.1 micrometres), but there is no problem in ensuring that the grain sizes of the materials of the present invention are such that the effect of grain size is essentially insignificant. In all samples prepared by the present inventors, the grain size was greater than 0.1 micrometre. Some dielectric properties are also influenced by piezoelectric effects. Piezoelectric effects cause elastic strains in ceramic materials. The main effects of these elastic strains are a restriction of the polarisation directions of neighbouring grains in the ferroelectric phase, and a broadening of the ferroelectric transition. These effects are of no importance in the implementation of the present invention, in which the material operates in the paraelectric phase. Also unimportant in the context of the present invention, although included in the theoretical treatment, is the fact that as the temperature of barium titanate is progressively reduced below the transition from its paraelectric state to its ferroelectric state, there are two further transitions (to a monoclinic crystal structure and to a rhombohedral structure).

The theory discussed above applies, with simple modification of the numerical parameters, both to first-order ferroelectric materials (for which there is an abrupt change in polarisation at the Curie temperature) and to second-order ferroelectric materials (for which there is no discontinuity in polarisation at the Curie temperature; the polarisation simply rises smoothly from zero as the temperature is lowered below T_c). The energy storage behaviour of first-order and second-order ferroelectric materials is similar and the present theory indicates no particular advantage or disadvantage associated with the nature of the ferroelectric phase transition for materials with otherwise similar dielectric parameters.

In other realisations of the present invention, produced and tested by the present inventors, the base material of the modified ceramic material and the additive comprised the following combinations:

(a) The base material was a mixture or combination of barium titanate and barium zirconate; the additive was a mixture or combination of strontium titanate and strontium zirconate; the atomic ratio of barium to strontium had various values in the range of from 0.2 to 0.8; and the atomic ratio of zirconium to titanium had various values from 0.1 to 0.5.

(b) The base material was lead titanate, lead zirconate or a mixture or combination of lead titanate and lead zirconate, and the additive was strontium titanate or strontium zirconate. When the base material was lead titanate and the additive was strontium titanate, it was found that particularly good results were obtained when the additive comprised from 50 mole per cent to 90 mole per cent of the modified ceramic material.

It will be appreciated from the foregoing discussion that these and the earlier recited combinations of base material and additive do not limit the scope of the present invention. They are practical combinations which are readily able to be implemented. The general requirements for the present invention are as follows:

1. The ceramic material to be modified should have a large Curie constant C, and a large spontaneous polarisation P_s.
2. The material to be modified must be capable of having its Curie temperature adjusted, by chemical additions, to a temperature well below the temperature at which capacitors including the modified material as a dielectric are to be used.
3. This adjustment of the Curie temperature should not unduly degrade either the spontaneous polarisation or the Curie constant.
4. The electrical breakdown strength of the modified material, and thus its attainable working field, should be as high as possible.

5. The optimal composition of the modified material can be determined from the theory on the basis of the way in which the Curie temperature, the spontaneous polarisation and the Curie constant vary with composition, and by the attainable working field.

There are other materials that can be added to barium titanate, in place of strontium titanate, to depress the Curie temperature. Among these are barium zirconate, barium stannate and barium hafnate. The approach disclosed above to optimising the performance of capacitors can be applied similarly to ceramic dielectric materials which are formed by adding these materials, individually or in combination with strontium titanate or with one another, to barium titanate. In particular, the approach allows a global optimum to be determined for the addition of all of these materials. It is to be expected that the energy storage achievable at this global optimum will exceed that obtainable with barium titanate modified by the addition of strontium titanate alone.

It should be noted that niobates and tantalates, which (in general) have a high spontaneous polarisation and thus appear to be candidates for modification to become materials in accordance with the present invention, do not at present qualify as candidate materials, for they have high Curie temperatures (around 1200°C) and there is no known additive which reduces the Curie temperature to a value below room temperature without substantially degrading the spontaneous polarisation.

In evaluating candidate materials for modification, it should also be noted (from Figure 1 and Figure 3) that the attainable energy density increases as the working field increases. The electric breakdown strength is a structure-sensitive property, amenable to improvement by trace additions and by modification of processing conditions. Thus the present invention also encompasses a modified ceramic dielectric material as defined earlier in this specification, with the addition of at least one further additive to improve its electrical breakdown strength. Such a further additive will be included as a finely-ground powder in the mixture that is formed into a slurry with an organic binder in the preparation of the modified ceramic material. Depending on the nature of the further additive, it will be distributed substantially uniformly within the modified ceramic material, or it will be concentrated in the grain boundary regions of the modified ceramic material.

CLAIMS

1. A modified ceramic material having a displacement ferroelectric transition suitable for use as a dielectric material in multi-layer capacitors, said modified ceramic material comprising a base material and an additive distributed therein, characterised in that
   (a) the base material is a ferroelectric ceramic material having (i) a ferroelectric Curie temperature which is either higher than or lower than the working temperature of said capacitors, (ii) a large value of spontaneous polarisation below its Curie temperature, and (iii) a large value of the Curie constant;
   (b) the additive is a material which (i) forms mixed crystals with the base material without changing its crystal structure, (ii) does not significantly decrease the spontaneous polarisation or the Curie constant of the base material, and (iii) reduces the Curie temperature of the base material;
   (c) the additive is distributed substantially uniformly within the base material; and
   (d) the amount of additive present in the modified ceramic material reduces the Curie temperature of the base material to a value at least 50°C below the working temperature.

2. A modified ceramic material as defined in claim 1, in which said base material has a perovskite crystal structure.

3. A modified ceramic material as defined in claim 2, in which said base material is barium titanate and said additive is a material selected from the group consisting of strontium titanate, barium zirconate, barium stannate, barium hafnate, and a mixture of two or more of these additives.

4. A modified ceramic material as defined in claim 2, in which said base material is barium titanate, said additive is strontium titanate, and said additive comprises from 40 mole per cent to 95 mole per cent of the modified ceramic material.

5. A modified ceramic material as defined in claim 4, in which said additive comprises from 50 mole per cent to 95 mole per cent of the modified ceramic material.

6. A modified ceramic material as defined in claim 4, in which said additive comprises 70 mole per cent to 90 mole per cent of the modified ceramic material.

7. A modified ceramic material as defined in claim 1, in which (i) said base material is a mixture of barium titanate and barium zirconate, (ii) said additive is a combination of strontium titanate and strontium zirconate, (iii) the atomic ratio of

barium to strontium in the modified ceramic material is in the range of from 0.2 to 0.8, and (iv) the atomic ratio of zirconium to titanium in the modified ceramic material is in the range of from 0.1 to 0.5.

8. A modified ceramic material as defined in claim 1, in which (i) said base material is selected from the group consisting of lead titanate, lead zirconate and a combination of lead titanate and lead zirconate, and (ii) said additive is strontium titanate or strontium zirconate.

9. A modified ceramic material, as defined in claim 8, in which said base material is lead titanate, said additive is strontium titanate, and said additive comprises from 50 mole per cent to 90 mole per cent of the modified ceramic material.

10. A modified ceramic material as defined in any preceding claim, in which the additive content is sufficient to reduce the Curie temperature of the base material to a value which is at least 100°C below the working temperature.

11. A modified ceramic material as defined in any preceding claim, further characterised in that said modified ceramic material includes a further additive, said further additive being either distributed substantially uniformly within the ceramic material or concentrated substantially at

the grain boundaries of the base material, said further additive being adapted to improve the electrical breakdown strength of said modified ceramic material.

12. A multi-layer capacitor comprising a plurality of layers of a dielectric material, interleaved with metallic electrodes, characterised in that said dielectric material is a modified ceramic material as defined in any one of claims 1 to 11.

13. A method of making a multi-layer capacitor as defined in claim 12, said method comprising the steps of
    (a) chemically precipitating a powder of said base material and said additive in pre-determined proportions;
    (b) grinding the precipitated powder to ensure that it contains small grains of substantially uniform size;
    (c) forming the ground powder mixture into a slurry with an organic binder;
    (d) casting the slurry on a moving belt and forming the cast slurry into a thin "green" tape with a doctor blade;
    (e) painting or printing electrodes on the "green" tape;
    (f) forming a plurality of tapes with electrodes thereon into a stack;
    (g) laminating the stack under pressure;

(h) heating the stack to a temperature sufficient to burn out the binder; and

(i) sintering the laminated stack.

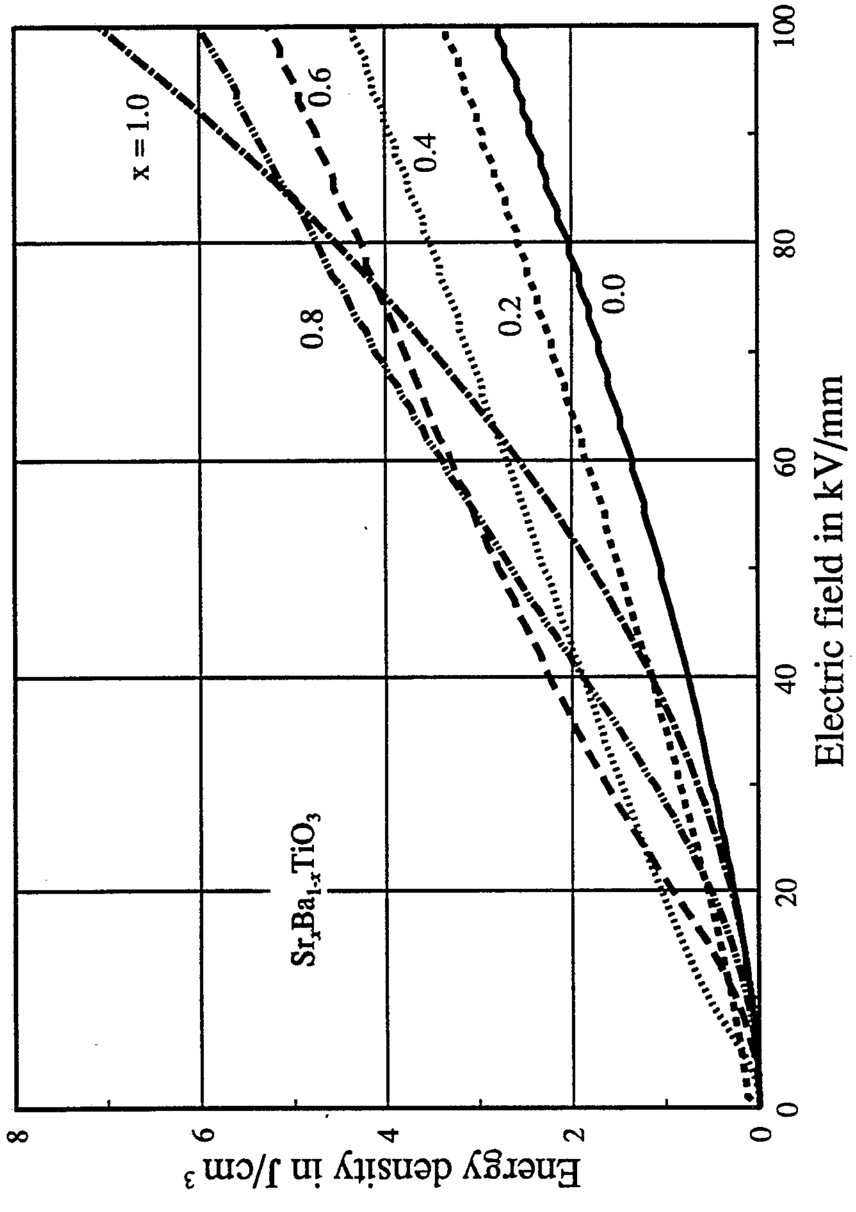
$Sr_xBa_{1-x}TiO_3$
x = 1.0
0.8
0.6
0.4
0.2
0.0
Energy density in J/cm ^{3}
0
2
4
6
8
Electric field in kV/mm
0
20
40
60
80
100

FIG. 1

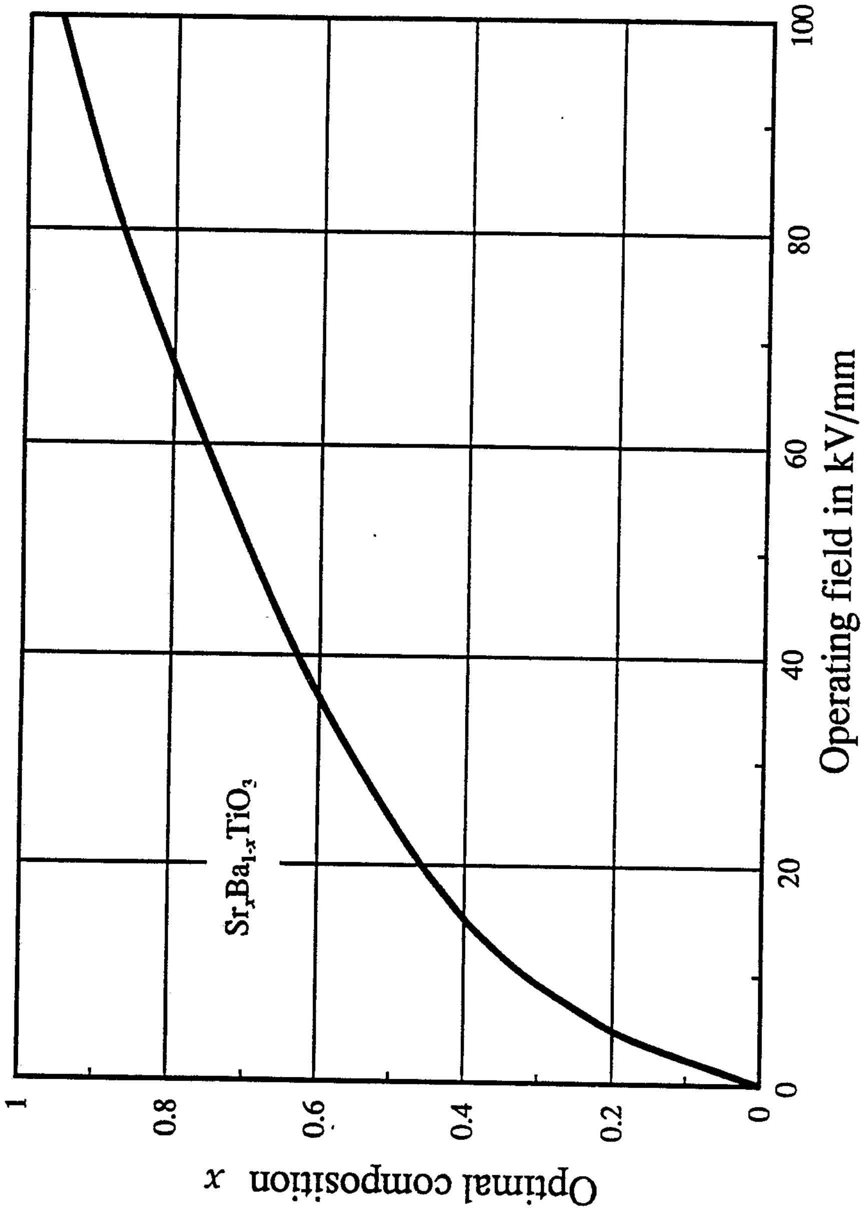
Optimal composition x
1
0.8
0.6
0.4
0.2
0
0
20
40
60
80
100
Operating field in kV/mm
$Sr_xBa_{1-x}TiO_3$

FIG. 2

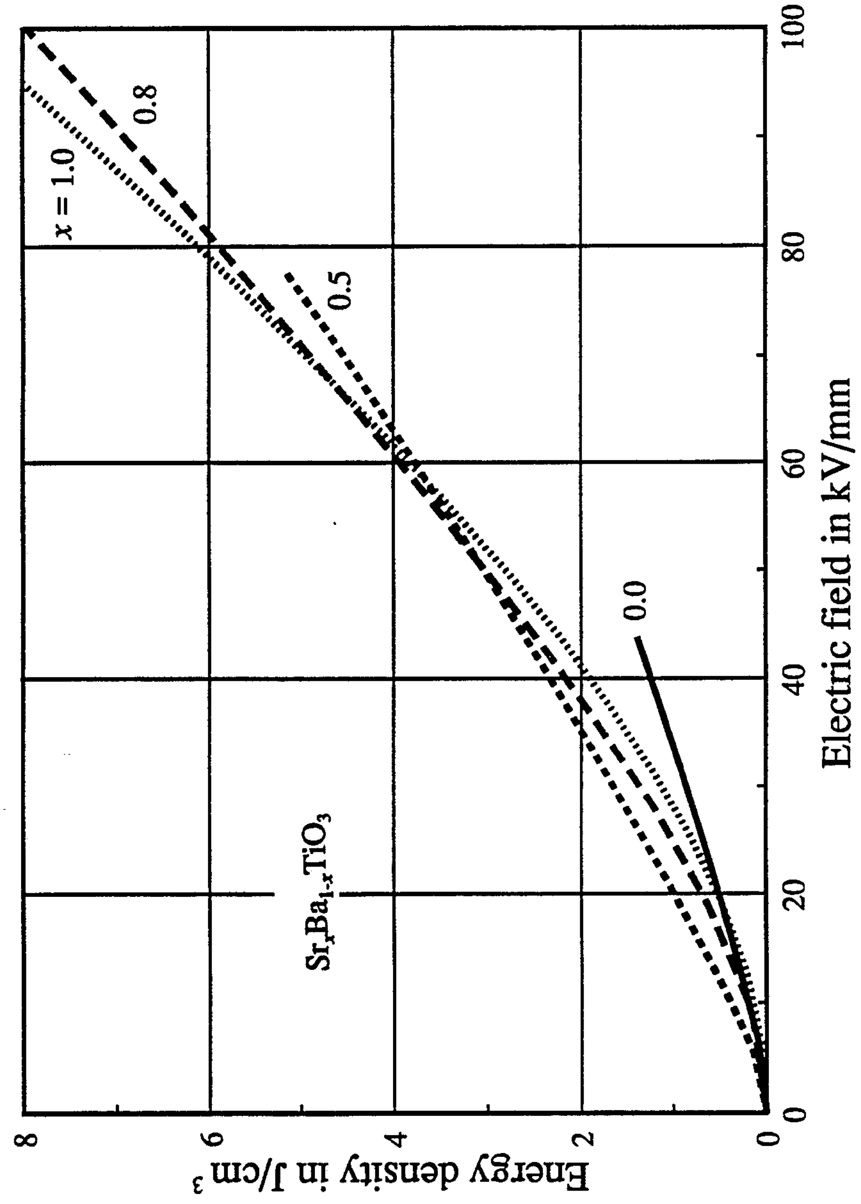
Energy density in J/cm^3
0
2
4
6
8
Electric field in kV/mm
0
20
40
60
80
100
$x = 1.0$
0.8
0.5
0.0
$Sr_xBa_{1-x}TiO_3$

FIG. 3

INTERNATIONAL SEARCH REPORT

International application No.
PCT/AU92/00644

A. CLASSIFICATION OF SUBJECT MATTER

Int. Cl.^{5} H01G 4/12 H01B 3/12

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC H01G 4/12 HO1B 3/12

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
AU : IPC as above

Electronic data base consulted during the international search (name of data base, and where practicable, search terms used)
DERWENT
JAPIO

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to Claim No.
X	US,A, 2467169 (WAINER) 12 April 1949 (12.04.49) column 2, lines 28-50, columns 3 and 4	1-6, 8-10
X	GB,A, 574577 (DUBILIER CONDENSER COMPANY LTD) 11 January 1946 (11.01.46) page 1 lines 54-80, page 3 lines 53-76	1-5, 8-10
X	US,A, 2402517 (WAINER) 18 June 1946 (18.06.46) columns 3-4	1-3

☒ Further documents are listed in the continuation of Box C.

☐ See patent family annex.

*	Special categories of cited documents :
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"Y"	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
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C(Continuation).	DOCUMENTS CONSIDERED TO BE RELEVANT	
Category*	**Citation of document, with indication, where appropriate of the relevant passages**	**Relevant to Claim No.**
X	US,A, 2402515 (WAINER) 18 June 1946 (18.06.46) column 4, tables 3 and 4	1-3
X	US,A, 2452532 (WAINER) 26 October 1948 (26.10.48) columns 3-4, table 1	1-3
X	GB,A, 583639 (EVERY) 23 December 1946 (23.12.46) page 4 tables 3 and 4, page 6 lines 41-61	1-3
X	GB,A, 599771 (EVERY) 19 March 1948 (19.03.48) page 2 table 1, page 4 lines 8-10	1-3
X	Derwent Abstract Accession No. 50500 A/28, Class L03, R25, R41, JP,A, 53-062200 (DAINI SEIKOSHA K.K.) 3 June 1978 (03.06.78) abstract	1-3
X	GB,A, 843920 (CLEVITE CORPORATION) 10 August 1960 (10.08.60) page 5 table 1, page 6 lines 69-76	1, 8
X	US,A, 2528113 (CARLSON et al) 31 October 1950 (31.10.50) column 2 line 3-8	1-3
X	AU,B, 23967/56 (217162) (N.V. PHILIPS GLOEILAMPENFABRIEKEN) 20 June 1956 (20.06.56) page 2 lines 5-14	1, 8