Electroceramics

Materials·properties·applications

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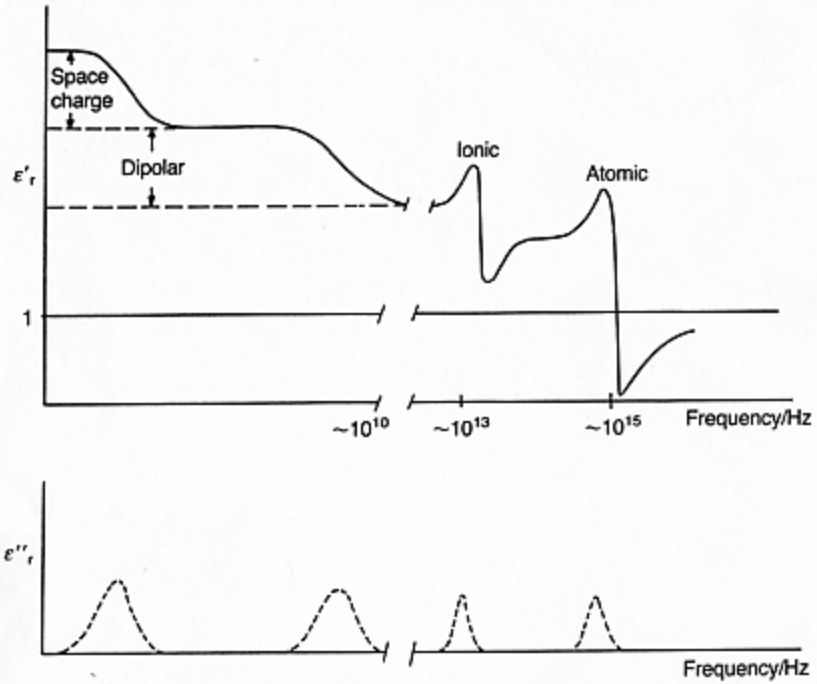


Fig. 2.38 Variation of ε'_r and ε''_r with frequency. Space charge and dipolar polarizations are relaxation processes and are strongly temperature dependent; ionic and electronic polarizations are resonance processes and sensibly temperature independent. Over critical frequency ranges energy dissipation is a maximum as shown by peaks in $\varepsilon''_r(\omega)$.

Table 2.5 Relationship between ε_r and n^2

	ε_r	n	n^2
Diamond	5.68	2.42	5.85
Germanium	≈ 16	4.09	16.73
NaCl	5.9	1.54	2.37
H_2O	≈ 80	1.33	1.77

2.7.3 Barium titanate – the prototype ferroelectric ceramic

Barium titanate, the first ceramic material in which ferroelectric behaviour was observed, is the ideal model for a discussion of the phenomenon from the point of view of crystal structure and microstructure.

$BaTiO_3$ is isostructural with the mineral perovskite ($CaTiO_3$) and so is referred to as 'a perovskite'. Above its Curie point (approximately 130 °C) the

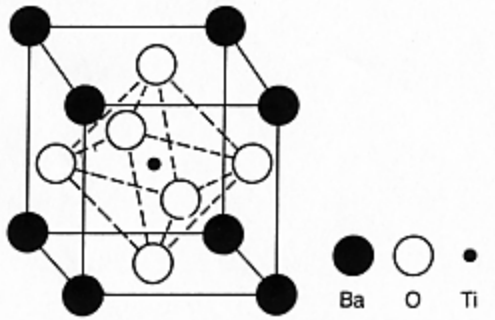
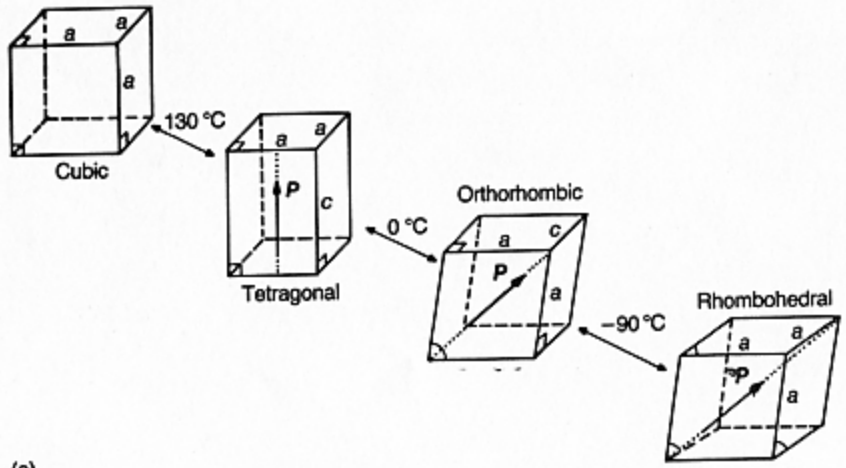


Fig. 2.39 The unit cell of $BaTiO_3$.

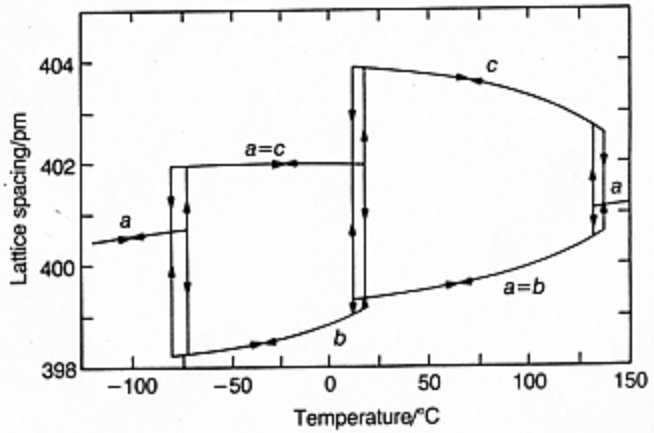
unit cell is cubic with the ions arranged as in Fig. 2.39. Below the Curie point the structure is slightly distorted to the tetragonal form with a dipole moment along the *c* direction. Other transformations occur at temperatures close to 0 °C and − 80 °C: below 0 °C the unit cell is orthorhombic with the polar axis parallel to a face diagonal and below − 80 °C it is rhombohedral with the polar axis along a body diagonal. The transformations are illustrated in Fig. 2.40(a), and the corresponding changes in the values of the lattice parameters, the spontaneous polarization and the relative permittivity are shown in Figs 2.40(b), 2.40(c) and 2.40(d).

A consideration of the ion displacements accompanying the cubic–tetragonal transformation can give insight into how the spontaneous polarization might be coupled from unit cell to unit cell. X-ray studies have established that in the tetragonal form, taking the four central (B) oxygen ions in the cubic phase as origin, the other ions are slightly shifted as shown in Fig. 2.41. It is evident that, if the central Ti^{4+} ion is closer to one of the O^{2-} ions marked A, it will be energetically favourable for the Ti^{4+} ion on the opposite side of A to be located more distantly from that O^{2-} ion, thus engendering a similar displacement of all the Ti^{4+} ions in a particular column in the same direction. Coupling between neighbouring columns occurs in $BaTiO_3$ so that all the Ti^{4+} ions are displaced in the same direction. In contrast, in the orthorhombic perovskite $PbZrO_3$ the Zr^{4+} ions in neighbouring columns are displaced in opposite senses so that the overall dipole moment is zero. Such a structure is termed *antiferroelectric* if the material shows a Curie point.

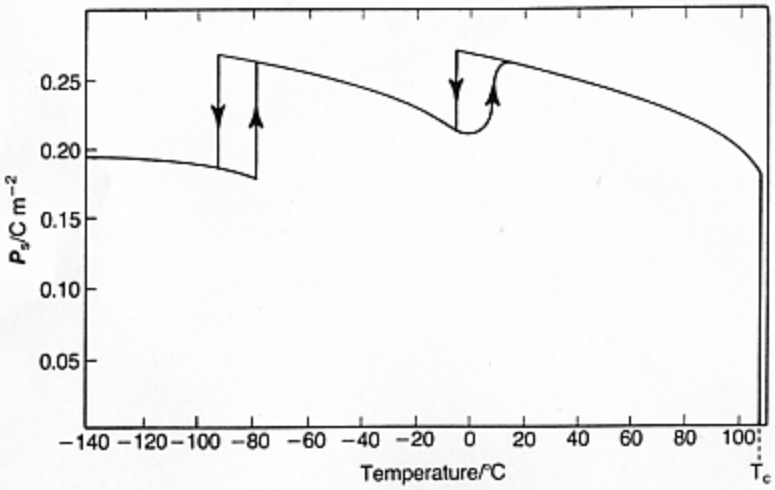
In tetragonal $BaTiO_3$ the energy of the Ti^{4+} ion in terms of its position along the *c* axis takes the form of two wells (Fig. 2.42). An applied field in the opposite direction to the polarization may enable a Ti^{4+} ion to pass over the energy barrier between the two states and so reverse the direction of the polarity at that point. When this happens the energy barriers for neighbouring ions are reduced and the entire region affected by the field will eventually switch into the new direction. A similar mechanism is available for changes of



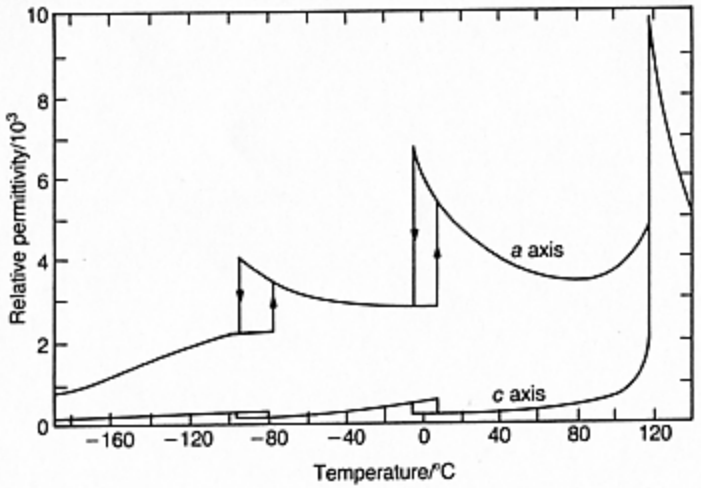
(a)



(b)



(c)



(d)

Fig. 2.40 Properties of single-crystal $BaTiO_3$: (a) unit-cell distortions of the polymorphs; (b) lattice dimensions versus temperature (after Clarke); (c) spontaneous polarization versus temperature; (d) relative permittivities measured in the *a* and *c* directions versus temperature (after Merz).

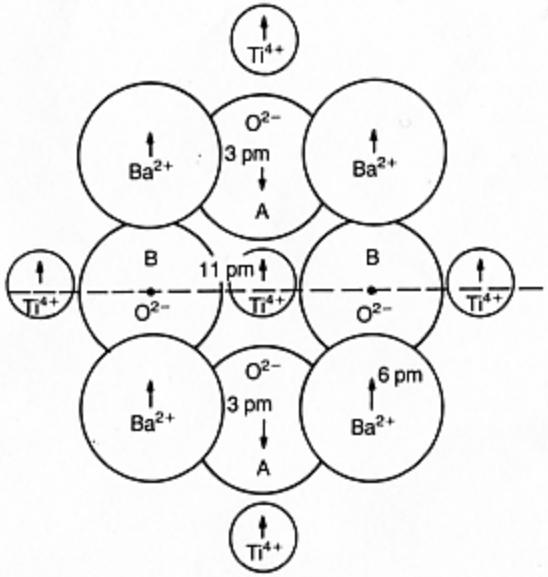


Fig. 2.41 Approximate ion displacements in the cubic–tetragonal distortion in $BaTiO_3$.

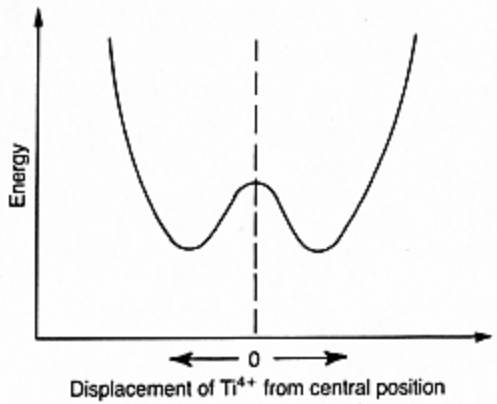


Fig. 2.42 Variation in the potential energy of Ti^{4+} along the *c* axis.

polarity through 90° but in this case there is an accompanying dimensional change because the polar *c* axis is longer than the non-polar *a* axis (Fig. 2.40(b)). Switching through 90° can be induced through the ferroelastic effect by applying a compressive stress along the polar axis without an accompanying electric field. Switching through 180° is unaffected by mechanical stress.

An immediate consequence of the onset of spontaneous polarization in a body is the appearance of an apparent surface charge density and an accompanying depolarizing field E_D as shown in Fig. 2.43(a). The energy associated with the polarization in the depolarizing field is minimized by twinning, a process in which the crystal is divided into many oppositely polarized regions, as shown in Fig. 2.43(b). These regions are called *domains* and the whole configuration shown comprises 180° domains. Thus the surface

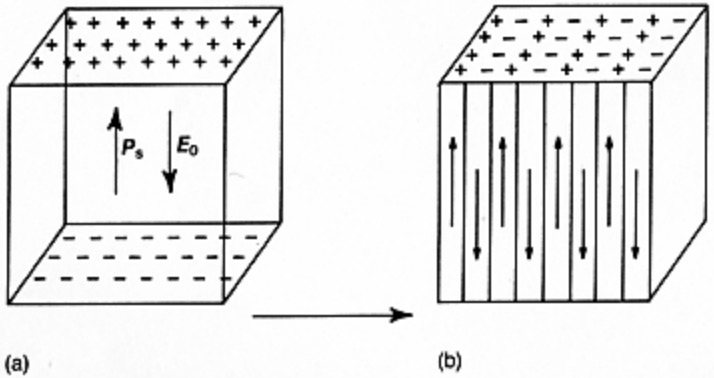


Fig. 2.43 (a) Surface charge associated with spontaneous polarization; (b) formation of 180° domains to minimize electrostatic energy.

consists of a mosaic of areas carrying apparent charges of opposite sign, resulting in a reduction in E_D and in energy. This multidomain state can usually be transformed into a single domain by applying a field parallel to one of the polar directions. The domains with their polar moment in the field direction grow at the expense of those directed oppositely until only a single domain remains. The presence of mechanical stress in a crystal results in the development of 90° domains configured so as to minimize the strain. For example, as ceramic $BaTiO_3$ cools through the Curie temperature individual crystallites are subjected to large mechanical stresses leading to the development of 90° domains. The configurations can be modified by imposing either an electric or a mechanical stress. A polycrystalline ceramic that has not been subjected to a static field behaves as a non-polar material even though the crystals comprising it are polar. One of the most valuable features of ferroelectric behaviour is that ferroelectric ceramics can be transformed into polar materials by applying a static field. This process is called 'poling'. The ceramic can be depoled by the application of appropriate electric fields or mechanical stresses. These poling and depoling processes are illustrated schematically in Fig. 2.44.

The random directions of the crystallographic axes of the crystallites of a ceramic limit the extent to which spontaneous polarization can be developed. It has been calculated that the fractions of the single-crystal polarization value that can be attained in a ceramic in which the polar axes take all possible alignments are 0.83, 0.91 and 0.87 for perovskites with tetragonal, orthorhombic or rhombohedral structures respectively. In ceramic tetragonal $BaTiO_3$ the saturation polarization is about half the single-crystal value. The value attainable is limited by the inhibition of 90° switching by internal strains although 180° switching can be almost complete.

The domain structure revealed by polishing and etching an unpoled ceramic specimen is shown in Fig. 2.45(a). The principal features in the form of parallel lines are due to 90° changes in the polar direction. The orientations occurring in a simple domain structure are shown schematically in Fig. 2.45(b). The thickness of the layer separating the domains, i.e. the domain wall, is of the order of 10 nm but varies with temperature and crystal purity. The wall energy is of the order $10\,mJ\,m^{-2}$.

The detailed geometry and dynamics of changes in domain configuration in a single crystal accompanying changes in applied field are complex and there is marked hysteresis between induced polarization and applied field. Conditions in a crystallite clamped within a ceramic are even more complex.

The hysteresis loop of a single-domain single crystal of $BaTiO_3$ is shown in Fig. 2.46(a). The almost vertical portions of the loop are due to the reversal of the spontaneous polarization as reverse 180° domains nucleate and grow. The almost horizontal portions represent saturated states in which the crystal is single domain with a permittivity ε_r of 160 (cf. Fig. 2.40(d)) obtainable in the polar direction. The coercive field at room temperature when the loop is

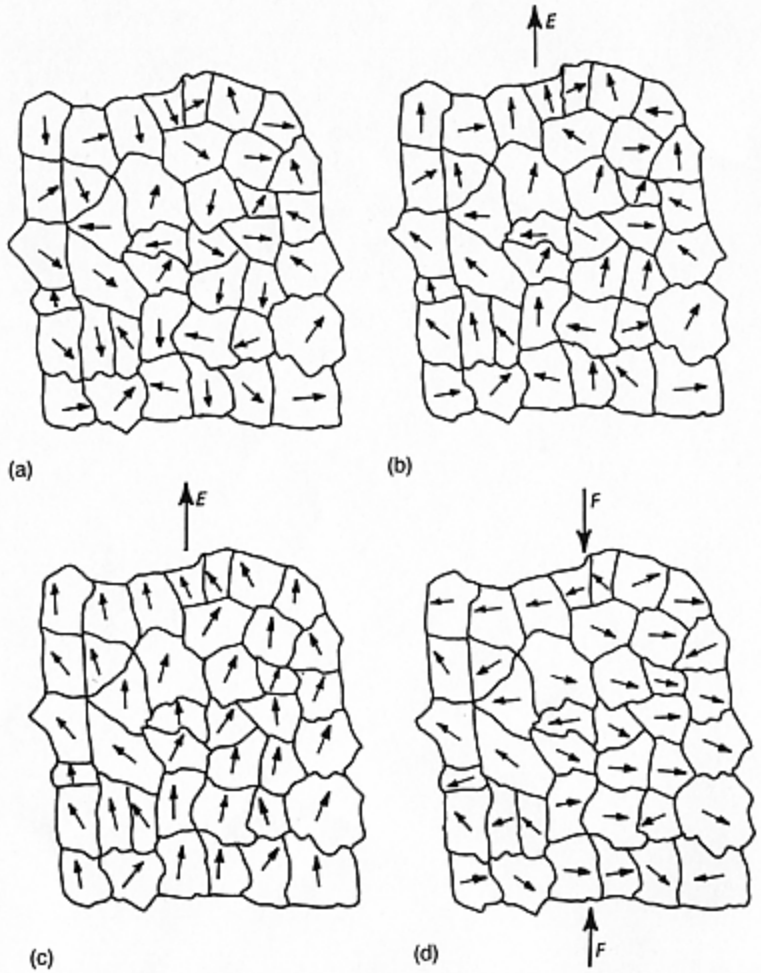
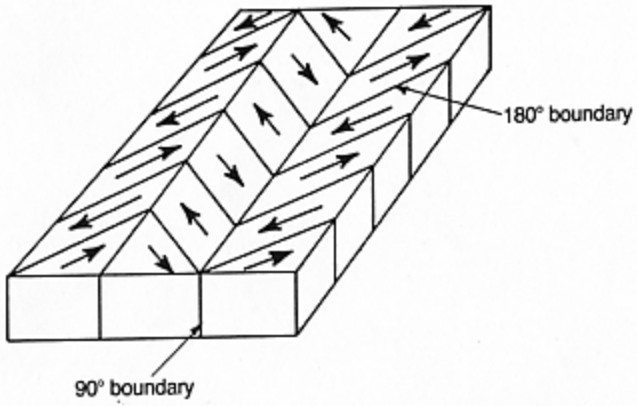


Fig. 2.44 Poling in a two-dimensional ceramic: (a) unoriented material; (b) oriented by 180° domain changes; (c) oriented by 180° and 90° domain changes; (d) disoriented by stress.

created by a 50 Hz supply is 0.1 MV m^{-1} and the saturation polarization is 0.27 C m^{-2}. When the field is reduced below 0.1 MV m^{-1} the loop shrinks, and at fields of about 1 V m^{-1} it becomes a narrow ellipse with its major axis parallel to the almost horizontal portion of the fully developed loop.

The hysteresis loop of a ceramic varies according to composition and ceramic structure but is typically of the form shown in Fig. 2.46(b). The coercive field is higher and the remanent polarization is lower than for a single crystal. Both 180° and 90° changes take place during a cycle and are impeded by the defects and internal strains within the crystallites.

(a)



(b)

Fig. 2.45 (a) Polished and etched surface of unpoled ceramic; (b) schematic diagram of 180° and 90° domains in barium titanate.

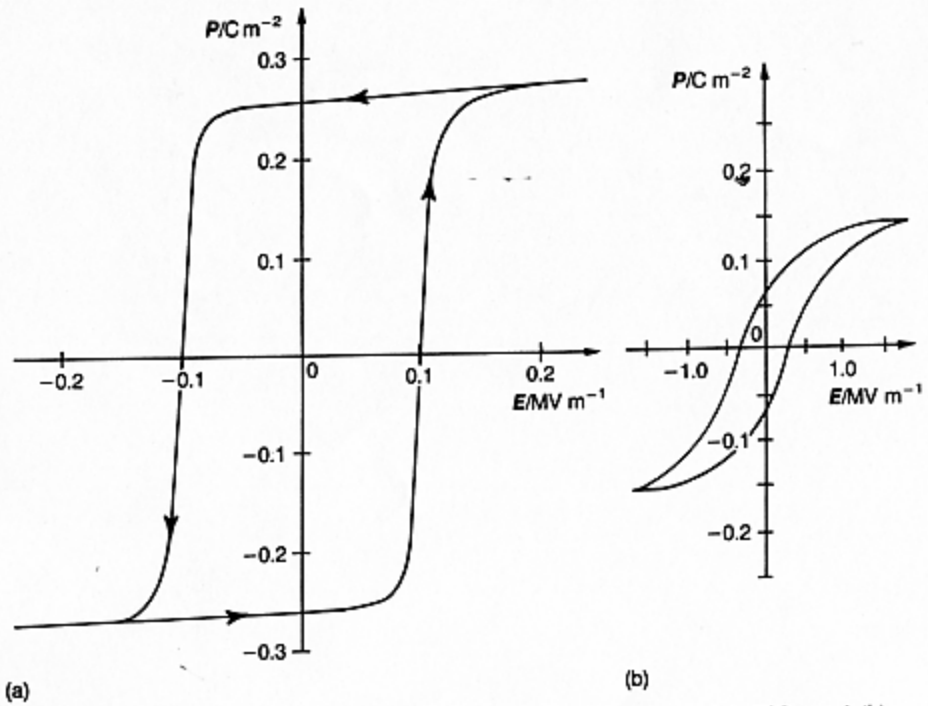


Fig. 2.46 Hysteresis loops for (a) a single-domain single crystal of $BaTiO_3$ and (b) $BaTiO_3$ ceramic.

The hysteresis loss is proportional to the area of the loop, so that for a single crystal taken around the loop in Fig. 2.46(a) it amounts to about 0.1 MJ m^{-3}. At 1000 Hz the power dissipated as heat would be 100 MW m^{-3} which would result in a very rapid rise in temperature. The dissipation factor in a ceramic is also very high at high fields, but at the 100 V mm^{-1} level tan δ becomes less than 0.1 for undoped material. Modifications to the composition diminish the loss still further.

A further unusual characteristic of ferroelectric materials is that their properties change with time in the absence of either external mechanical or electrical stresses or temperature changes. This is due to a diminution of domain wall mobility through the gradual build-up of inhibiting structures. These may be internal fields due to the alignment of dipoles formed from lattice defects and impurity ions, the redistribution of internal strains due to crystal anisotropy or the accumulation of defects in the domain walls.

The rate of change $\partial p/\partial t$ of a property with time is approximately inversely proportional to the time after a specimen has cooled from above its Curie point to room temperature:

$$\frac{\partial p}{\partial t} = \frac{a'}{t} \tag{2.119}$$

On integration equation (2.119) yields

$$p = a \log_{10}\left(\frac{t}{t_0}\right) \tag{2.120}$$

where $a = a' \log_e 10$ and t_0 is an arbitrary zero for the time. a is usually less than 0.05 for most properties of commercial materials. It varies in sign according to the property and, for instance, is negative for permittivity and positive for Young's modulus. The value of a is often given as a percentage per decade, which implies that the change in a property will be the same between 1 and 10 days as between 100 and 1000 days. The effect therefore becomes negligible after a sufficient lapse of time provided that the component is not subjected to high mechanical or electrical stresses or to temperatures near to or exceeding the Curie point. Such stresses will disturb the domain structure and consequently the ageing rate will increase to a value above that expected from equation (2.119).

One very significant advantage of ceramic ferroelectrics is the ease with which their properties can be modified by adjusting the composition and the ceramic microstructure. Additions and the substitution of alternative cations can have the following effects:

1. shift the Curie point and other transition temperatures;
2. restrict domain wall motion;
3. introduce second phases or compositional heterogeneity;
4. control crystallite size;
5. control the oxygen content and the valency of the Ti ion.

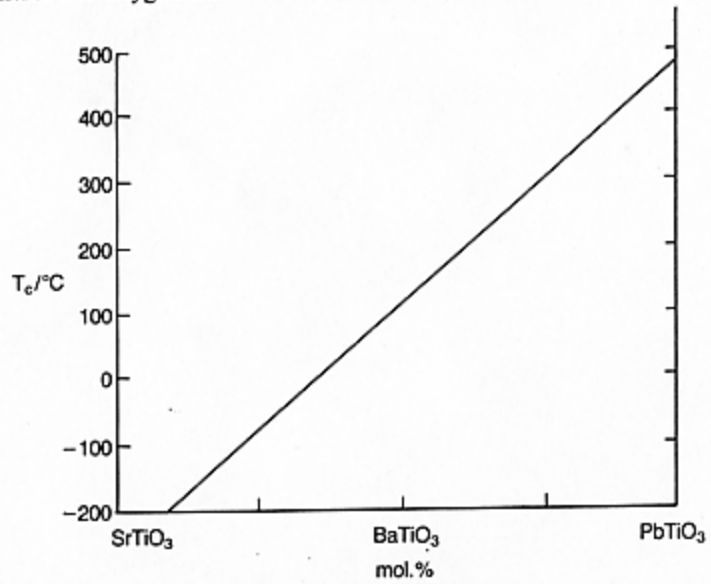


Fig. 2.47 The effect on the Curie point of the substitution of either strontium or lead for barium in $BaTiO_3$.

The effects are important for the following reasons.

1. Changing the Curie point enables the peak permittivity to be put in a temperature range in which it can be exploited. The substitution of Sr^{2+} for Ba^{2+} in $BaTiO_3$ lowers T_c whilst the substitution of Pb^{+} increases it, as shown in Fig. 2.47.
2. A number of transition ions (Fe^{3+}, Ni^{2+}, Co^{3+}) that can occupy Ti^{4+} sites reduce that part of the dissipation factor due to domain wall motion.
3. Broadening of the permittivity–temperature peak can be effected by making additions, such as $CaZrO_3$ to $BaTiO_3$. The resultant materials may contain regions of variable composition that contribute a range of Curie points so that the high permittivity is spread over a wider temperature range, although at a somewhat lower level than that of the single peak.
4. Cations that have a higher valency than those they replace, when present at levels exceeding about 0.5 cat. %, e.g. La^{3+} in place of Ba^{2+} or Nb^{5+} in place of Ti^{4+}, generally inhibit crystal growth. This has the effect of raising the permittivity level below the Curie point as shown in Fig. 2.48. Crystal size is also controlled by sintering conditions. It has important effects on the electro-optical behaviour.
5. Higher-valency substituents at low concentrations (< 0.2 cat. %) in $BaTiO_3$ lead to low resistivity. However, lower-valency substituents, such as Mn^{3+} on Ti^{4+} sites, act as acceptors and enable high-resistivity dielectrics to be sintered in atmospheres with low oxygen contents.

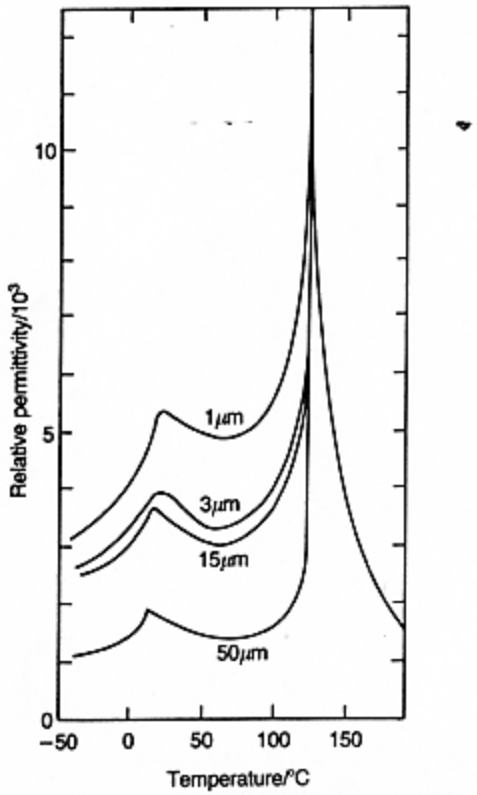


Fig. 2.48 The effect of grain size on the permittivity of a $BaTiO_3$ ceramic. (After Kinoshita and Yamaji.)

Applications Ferroelectric ceramics find applications in capacitors, infrared detection, sound detection in air and water, the generation of ultrasonic energy, light switches, current controllers and small thermostatic devices. In all these cases some aspects of their ferroelectric activity have to be suppressed and others enhanced. A suitable compromise is achieved by a combination of composition and ceramic structure as described in the relevant sections.

2.7.4 Mixtures of dielectrics

The properties of mixtures of phases depend on the distribution of the components. The concept of 'connectivity' is useful in classifying different types of mixture. The basis of this concept is that any phase in a mixture may be self-connected in zero, one, two or three dimensions. Thus randomly dispersed and separated particles have a connectivity of 0 while the medium surrounding them has a connectivity of 3. A disc containing a rod-shaped phase extending between its major surfaces has a connectivity of 1 with respect to the rods and of 3 with respect to the intervening phase. A mixture consisting of a stack of plates of two different phases extending over the entire area of the body has a connectivity of 2–2. In all, 10 different connectivities are possible for mixtures of two phases (0–0, 1–0, 2–0, 3–0, 1–1, 2–1, 3–1, 2–2, 3–2, 3–3). There are 20 possibilities for mixtures of three phases and 35 for mixtures of four phases.

The commonest case to have been analysed is that of 3–0 systems. James Clerk Maxwell (1831–1879) deduced that the permittivity ε_m of a random dispersion of spheres of permittivity ε_1 in a matrix of relative permittivity ε_2 is given by

$$\varepsilon_m = \varepsilon_2 \left\{ 1 + \frac{3V_f(\varepsilon_1 - \varepsilon_2)}{\varepsilon_1 + 2\varepsilon_2 - V_f(\varepsilon_1 - \varepsilon_2)} \right\} \tag{2.121}$$

where V_f is the volume fraction occupied by the dispersed particles. The result is independent of the size of the dispersed particles. For $\varepsilon_2 \gg \varepsilon_1$ and $V_f \leqslant 0.1$ equation (2.121) reduces to

$$\varepsilon_m = \varepsilon_2 \left(\frac{1 - 3V_f}{2} \right) \tag{2.122}$$