

Table 1.16 *Some compounds with the CdCl<sub>2</sub> structure. (Data taken from Wyckoff, 1971, Vol. 1)*

	<i>a</i> (Å)	<i>c</i> (Å)		<i>a</i> (Å)	<i>c</i> (Å)
CdCl <sub>2</sub>	3.854	17.457	NiCl <sub>2</sub>	3.543	17.335
CdBr <sub>2</sub>	3.95	18.67	NiBr <sub>2</sub>	3.708	18.300
CoCl <sub>2</sub>	3.544	17.430	NiI <sub>2</sub>	3.892	19.634
FeCl <sub>2</sub>	3.579	17.536	ZnBr <sub>2</sub>	3.92	18.73
MgCl <sub>2</sub>	3.596	17.589	ZnI <sub>2</sub>	4.25	21.5
MnCl <sub>2</sub>	3.686	17.470	Cs <sub>2</sub> O*	4.256	18.99

\*Cs<sub>2</sub>O has an anti-CdCl<sub>2</sub> structure.

The structure of Cs<sub>2</sub>O is unusual since it may be regarded as an anti-CdCl<sub>2</sub> structure (as in fluorite and antiferroite structures). Cs<sup>+</sup> ions form cubic close packed layers and oxide ions occupy the octahedral sites between alternate pairs of caesium layers. This raises some interesting questions because caesium is the most electropositive element and caesium salts are usually regarded as highly ionic. However, the structure of Cs<sub>2</sub>O clearly shows that Cs<sup>+</sup> ions are not surrounded by anions, as expected for an ionic structure, but have only three oxide neighbours, all located at one side. The structure is held together, in three dimensions, by bonding between caesium ions in adjacent layers.

It may be that the structure of Cs<sub>2</sub>O does not reflect any peculiar type of bonding but rather that it is the only structural arrangement which is feasible for a compound of this formula and for ions of this size. Thus, from the formula, the coordination numbers of Cs<sup>+</sup> and O<sup>2-</sup> must be in the ratio of 1:2; since Cs<sup>+</sup> is considerably larger than O<sup>2-</sup>, the maximum possible coordination number of oxygen by caesium may be six, which then leads to a coordination number of three for Cs<sup>+</sup>.

A related question arises with the structures of the other alkali oxides, in particular K<sub>2</sub>O and Rb<sub>2</sub>O. These have the antiferroite structure with coordination numbers of four and eight for M<sup>+</sup> and O<sup>2-</sup>, respectively. These compounds are unusual since Rb<sup>+</sup> is normally far too large a cation to enter into tetrahedral coordination with oxygen. However, if there is no feasible alternative structure, then perhaps Rb<sup>+</sup> ions have no choice but to enter the tetrahedral sites. With Cs<sub>2</sub>O, tetrahedral coordination of Cs<sup>+</sup> by O<sup>2-</sup> is probably impossible and hence it adopts the anti-CdCl<sub>2</sub> structure rather than the antiferroite structure. Thermodynamic data support these observations since neither Cs<sub>2</sub>O nor Rb<sub>2</sub>O are very stable: they oxidize readily to give peroxides, M<sub>2</sub>O<sub>2</sub>, and superoxides, MO<sub>2</sub>, which contain much larger anions.

### Perovskite (SrTiO<sub>3</sub>)

This very important structure type, of general formula ABX<sub>3</sub>, has a primitive cubic unit cell, shown in Fig. 1.36 as a projection down one axis (a) and as an oblique projection (b). It contains Ti at the cube corners (coordinates 0, 0, 0), Sr at

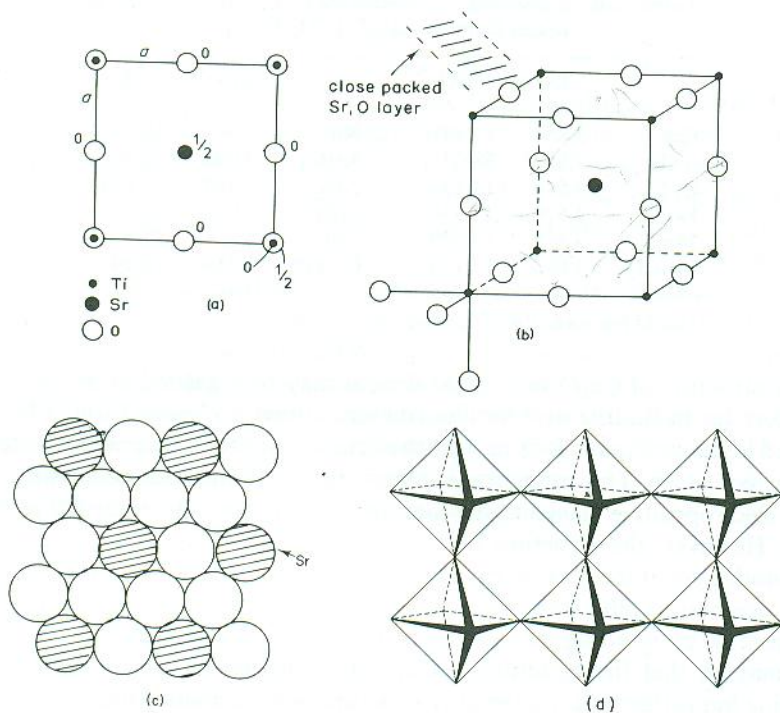


Fig. 1.36 The perovskite structure of  $\text{SrTiO}_3$

the body centre  $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$  and oxygen at the edge centres  $(\frac{1}{2}, 0, 0)$ ;  $(0, \frac{1}{2}, 0)$ ;  $(0, 0, \frac{1}{2})$ . The coordination environment of each atom may be seen in (b) and interatomic distances calculated by simple geometry. The octahedral coordination by oxygen of one of the corner titaniums is shown. The Ti—O bond length  $= a/2 = 1.953 \text{ \AA}$ . The strontium in the cube centre is equidistant from all twelve oxygens at the centres of the edges of the unit cell. The strontium—oxygen distance is equal to half the diagonal of any cell face, i.e.  $a/\sqrt{2}$  or  $2.76 \text{ \AA}$  (from the geometry of triangles, the length of a cell face diagonal is equal to  $\sqrt{a^2 + a^2}$ ).

Each oxygen has two titaniums as its nearest cationic neighbours, at a distance of  $1.953 \text{ \AA}$ , and four strontium atoms, coplanar with the oxygen at a distance of  $2.76 \text{ \AA}$ . However, eight other oxygens are at the same distance,  $2.76 \text{ \AA}$ , as the four strontiums. It is debatable whether the oxygen coordination number is best regarded as two (linear) or as six (a grossly squashed octahedron with two short and four long distances) or as fourteen (six cations and eight oxygens). No firm recommendation is made!

Having arrived at the unit cell of  $\text{SrTiO}_3$ , the atomic coordinates, coordination numbers and bond distances, we now wish to view the structure on a rather larger scale. There are several questions which may be asked. Does the structure have a close packed anion arrangement? Can the structure be regarded as some kind of



framework with atoms in the interstices? Answers to these questions are as follows.

Perovskite does not contain close packed oxide ions as such but the oxygens and strontiums, considered together, do form a cubic close packed array with the layers parallel to the  $\{111\}$  planes (Fig. 1.36b and c). To see this, compare the perovskite structure with that of NaCl (Fig. 1.2). The latter contains  $\text{Cl}^-$  ions at the edge centre and body centre positions of the cell and is cubic close packed. By comparison, perovskite contains  $\text{O}^{2-}$  ions at the edge centres and  $\text{Sr}^{2+}$  at the body centre. The structure of the mixed Sr, O close packed layers in perovskite is such that one quarter of the atoms are strontium, arranged in a regular fashion (Fig. 1.36c).

It is quite common for fairly large cations, such as  $\text{Sr}^{2+}$  ( $r = 1.1 \text{ \AA}$ ) to play apparently different roles in different structures, i.e. as twelve coordinate packing ions in perovskite or as octahedrally coordinated cations within a close packed oxide array, as in SrO (rock salt structure).

The formal relation between rock salt and perovskite also includes the  $\text{Na}^+$  and  $\text{Ti}^{4+}$  cations as both are in octahedral sites. Whereas in NaCl all octahedral sites are occupied (corners and face centres), in perovskite only one quarter (the corner sites) are occupied.

Perovskite may also be regarded as a framework structure constructed from corner-sharing ( $\text{TiO}_6$ ) octahedra and with  $\text{Sr}^{2+}$  ions placed in twelve-coordinate interstices. The octahedral coordination of one titanium is shown in Fig. 1.36b; each oxygen of this octahedron is shared with one other octahedron, such that the Ti–O–Ti arrangement is linear. In this way, octahedra are linked at their corners to form sheets (d), and neighbouring sheets are linked similarly to form a three-dimensional framework.

Several hundred oxides and halides form the perovskite structure; a selection is given in Table 1.17. The oxides contain two cations, whose combined oxidation state is six; several cation combinations are therefore possible.

As well as the cubic perovskite structure, described above, a variety of

Table 1.17 *Some compounds with the perovskite structure*

Compound	$a(\text{\AA})$	Compound	$a(\text{\AA})$
$\text{KNbO}_3$	4.007	$\text{SrTiO}_3$	3.9051
$\text{KTaO}_3$	3.9885	$\text{SrZrO}_3$	4.101
$\text{KIO}_3$	4.410	$\text{SrHfO}_3$	4.069
$\text{NaNbO}_3$	3.915	$\text{SrSnO}_3$	4.0334
$\text{NaWO}_3$	3.8622	$\text{SrThO}_3$	
$\text{LaCoO}_3$	3.824	$\text{CsCaF}_3$	4.522
$\text{LaCrO}_3$	3.874	$\text{CsCdBr}_3$	5.33
$\text{LaFeO}_3$	3.920	$\text{CsCdCl}_3$	5.20
$\text{LaGaO}_3$	3.875	$\text{CsHgBr}_3$	5.77
$\text{LaVO}_3$	3.99	$\text{CsHgCl}_3$	5.44

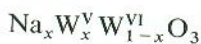
distorted, non-cubic structures exist, with tetragonal, rhombohedral, monoclinic, etc., symmetry. These lower-symmetry structures form on cooling the high-temperature cubic structures. Their structures are similar to the cubic perovskite structure, but the framework of octahedra may be slightly twisted or distorted. Some have interesting and useful properties, such as ferroelectricity (Chapter 7).

### Rhenium trioxide ( $\text{ReO}_3$ ) and tungsten bronzes

These structures are closely related to perovskite described above. The cubic  $\text{ReO}_3$  structure is the same as perovskite,  $\text{SrTiO}_3$ , but without the body centre Sr atoms. Its unit cell contains Re at corners with oxygen at edge centres. The  $\text{ReO}_6$  octahedra link up at their corners to form a three-dimensional framework, similar to that formed by the  $\text{TiO}_6$  octahedra in perovskite, but now the 12-coordinate cavities are empty.

A few oxides and halides form the  $\text{ReO}_3$  structure, Table 1.18, together with an example of the anti- $\text{ReO}_3$  structure in  $\text{Cu}_3\text{N}$ .

The *tungsten bronze* structure is intermediate between that of  $\text{ReO}_3$  and perovskite. It occurs in the series,  $\text{Na}_x\text{WO}_3$ . It comprises a three-dimensional framework of  $\text{WO}_6$  octahedra, as in  $\text{ReO}_3$ , but with some ( $0 < x < 1$ ) of the 12-coordinate sites occupied by Na. To accommodate this variation in stoichiometry,  $x$ , the oxidation state of tungsten is a mixture of V and VI. The formula of the bronzes may be written more completely as



The tungsten bronzes have interesting electrical properties. At low  $x$ , the materials are pale green/yellow in colour and are semiconducting. As  $x$  rises and electrons begin to occupy the  $5d$  band of tungsten, the materials become electrically conducting and exhibit metallic lustre, hence the name 'bronze'.

A wide variety of monovalent cations enter this structure; similar series occur with  $\text{MoO}_3$  in the *molybdenum bronzes*.

Table 1.18 Some compounds with the  $\text{ReO}_3$  structure

Compound	$a(\text{\AA})$
$\text{ReO}_3$	3.734
$\text{UO}_3$	4.156
$\text{MoF}_3$	3.8985
$\text{NbF}_3$	3.903
$\text{TaF}_3$	3.9012
$\text{Cu}_3\text{N}$	3.807



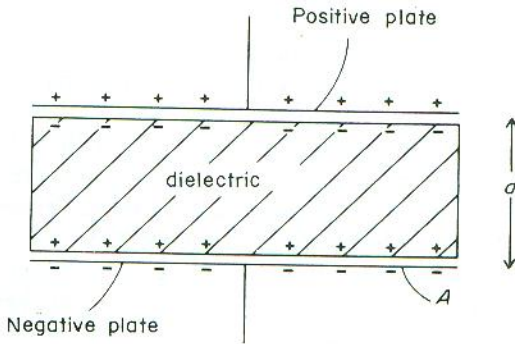


Fig. 7.35 Dielectric material between the plates of a parallel plate capacitor

a large, residual polarization of charge after the electric field has been removed.

Dielectric properties may be defined by the behaviour of the material in a parallel plate capacitor. This is a pair of conducting plates, parallel to one another and separated by a distance,  $d$ , that is small compared with the linear dimensions of the plates (Fig. 7.35). With a vacuum between the plates, the capacitance  $C_0$  is defined as

$$C_0 = \frac{e_0 A}{d} \quad (7.19)$$

where  $e_0$  is the permittivity of free space,  $8.854 \times 10^{-12} \text{ F m}^{-1}$ , and  $A$  is the area of the plates. Since  $e_0$  is constant, the capacitance depends only on the dimensions  $A$  and  $d$  of the capacitor. On applying a potential difference,  $V$ , between the plates, a quantity of charge,  $Q_0$ , is stored on them, given by

$$Q_0 = C_0 V \quad (7.20)$$

If a dielectric substance is now placed between the plates and the same potential difference applied, the amount of charge stored increases to  $Q_1$  and the capacitance therefore increases to  $C_1$ . The dielectric constant or relative permittivity,  $\epsilon'$ , of the dielectric is related to this increase in capacitance by

$$\epsilon' = \frac{C_1}{C_0} \quad (7.21)$$

The magnitude of  $\epsilon'$  depends on the degree of polarization or charge displacement that can occur in the material. For air,  $\epsilon' \approx 1$ . For most ionic solids,  $\epsilon' = 5$  to  $10$ . For ferroelectric materials such as  $\text{BaTiO}_3$ ,  $\epsilon' = 10^3$  to  $10^4$ .

### Ferroelectricity

Ferroelectric materials are distinguished from ordinary dielectrics by (a) their extremely large permittivities and (b) the possibility of retaining some residual

electrical polarization after an applied voltage has been switched off. As the potential difference applied across a dielectric substance is increased, a proportional increase in the induced polarization,  $P$ , or stored charge,  $Q$ , occurs. With ferroelectrics, this simple linear relation between  $P$  and  $V$  does not hold, as shown in Fig. 7.36. Instead, more complicated behaviour with a *hysteresis loop* is observed. The polarization behaviour that is observed on increasing the voltage is not reproduced on subsequently decreasing the voltage. Ferroelectrics exhibit a *saturation polarization*,  $P_s$ , at high field strength (for  $\text{BaTiO}_3$ ,  $P_s = 0.26 \text{ C m}^{-2}$  at  $23^\circ\text{C}$ ) and a *remanent polarization*,  $P_R$ , which is the value retained as  $V$  is reduced to zero after saturation. In order to reduce the polarization to zero, a reverse field is required; this is the *coercive field*,  $E_c$ .

Some common ferroelectric materials are listed in Table 7.3. All are characterized by structures in which one type of cation present, e.g.  $\text{Ti}^{4+}$  in  $\text{BaTiO}_3$ , can undergo a significant displacement, e.g.  $0.1 \text{ \AA}$ , relative to its anionic neighbours. These charge displacements give rise to dipoles and the high dielectric constants that are characteristic of ferroelectrics.

The unit cell of  $\text{SrTiO}_3$ , which has the same perovskite structure as  $\text{BaTiO}_3$ , is shown in Fig. 1.36. In the primitive cubic unit cell, titanium ions occupy corner

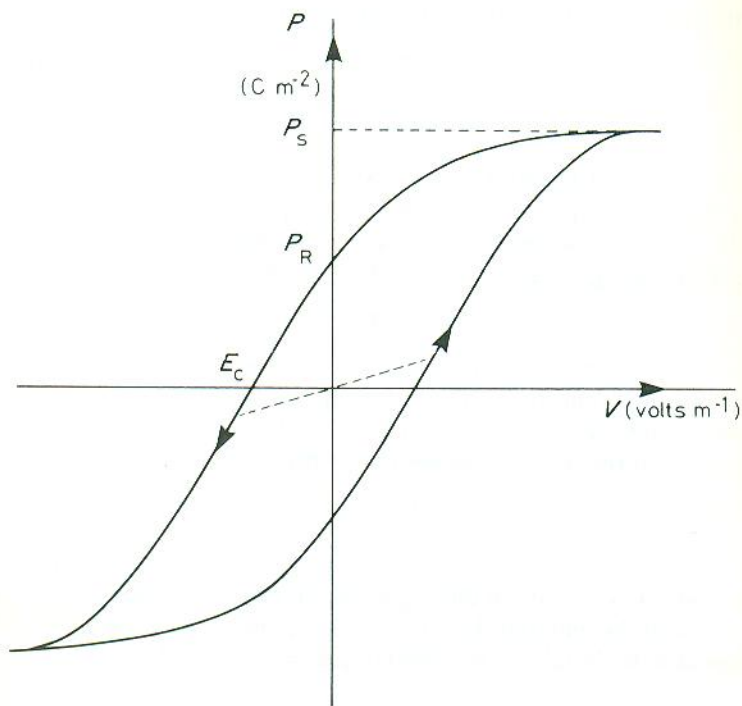


Fig. 7.36 Hysteresis loop of a ferroelectric. The dashed line passing through the origin represents the behaviour of normal dielectric materials

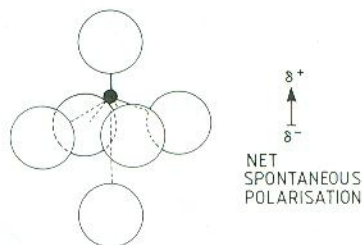
Table 7.3 Some ferroelectric materials

	$T_c(^{\circ}\text{C})$
Barium titanate, $\text{BaTiO}_3$	120
Rochelle salt, $\text{KNaC}_4\text{H}_4\text{O}_6 \cdot 4\text{H}_2\text{O}$	Between $-18$ and $+24$
Potassium niobate, $\text{KNbO}_3$	434
Potassium dihydrogen phosphate, KDP, $\text{KH}_2\text{PO}_4$	$-150$
Lead titanate, $\text{PbTiO}_3$	490
Lithium niobate, $\text{LiNbO}_3$	1210
Bismuth titanate, $\text{Bi}_4\text{Ti}_3\text{O}_{12}$	675
Gadolinium molybdate, GMO, $\text{Gd}_2(\text{MoO}_4)_3$	159
Lead zirconate titanate, PZT, $\text{Pb}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$	Depends on $x$

positions, oxygen ions occupy the cube edge centres and strontium is at the cube body centre. The structure is composed of  $(\text{TiO}_6)$  octahedra which link together by sharing corners to form a three-dimensional framework; strontium ions occupy twelve coordinate cavities within this framework.

This ideal, cubic, perovskite structure, which is stable above  $120^{\circ}\text{C}$  in  $\text{BaTiO}_3$ , does not possess a net dipole moment since the charges are symmetrically positioned. The material therefore behaves as a normal dielectric, albeit with a very high dielectric constant. Below  $120^{\circ}\text{C}$ , structural distortion occurs in  $\text{BaTiO}_3$ . The  $\text{TiO}_6$  octahedra are no longer regular because titanium is displaced off its central position and in the direction of one of the apical oxygens (Fig. 7.37). This gives rise to a spontaneous polarization. If a similar parallel displacement occurs in all of the  $\text{TiO}_6$  octahedra, a net polarization of the solid results.

In ferroelectric  $\text{BaTiO}_3$ , the individual  $\text{TiO}_6$  octahedra are polarized all of the time; the effect of applying an electric field is to persuade the individual dipoles to align themselves with the field. When complete alignment of all the dipoles occurs the condition of saturation polarization is reached. From the observed magnitude of  $P_s$ , it has been estimated that titanium is displaced by  $\sim 0.1 \text{ \AA}$  off the



**Fig. 7.37** Spontaneous polarization of a  $\text{TiO}_6$  octahedron in  $\text{BaTiO}_3$ . Note that in principle, there are six equivalent orientations in which this can occur



centre of its octahedron and in the direction of one of the oxygens. This has been confirmed by X-ray crystallography. This distance of  $0.1 \text{ \AA}$  or  $10 \text{ pm}$  is fairly small when compared with the average Ti—O bond distance of  $\sim 1.95 \text{ \AA}$  in  $\text{TiO}_6$  octahedra. Alignment of dipoles is shown schematically in Fig. 7.38(a); each arrow represents one distorted  $\text{TiO}_6$  octahedron and all are shown with a common direction of distortion.

In ferroelectrics such as  $\text{BaTiO}_3$ , *domain structures* form because adjacent  $\text{TiO}_6$  dipoles tend to align themselves parallel to each other (Fig. 7.39). The domains are of variable size but are usually quite large, tens or hundreds of

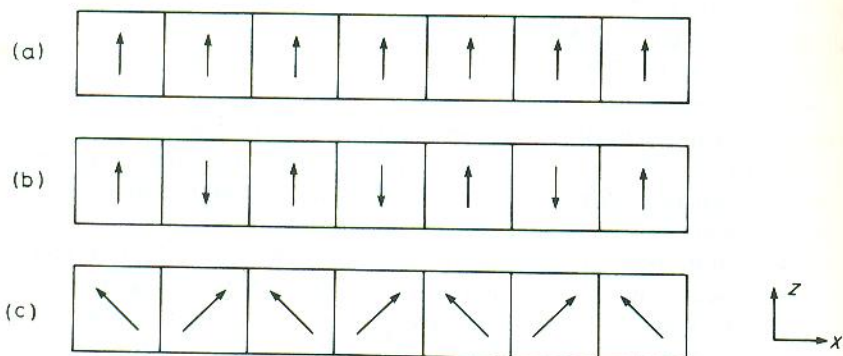


Fig. 7.38 Dipole orientation (schematic) in (a) a ferroelectric, (b) an antiferroelectric and (c) a ferrielectric

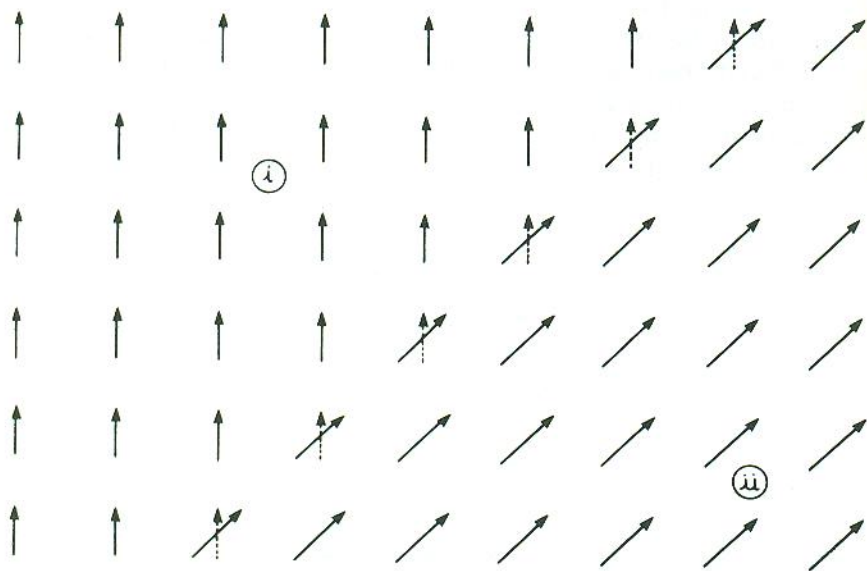


Fig. 7.39 Ferroelectric domains separated by a domain wall or boundary



ångstroms across. Within a single domain, the polarization of the dipoles has a common crystallographic direction. The net polarization of a piece of ferroelectric material is the vector resultant of the polarizations of the individual domains.

Application of an electric field across a ferroelectric leads to a change in the net polarization. This can arise from several possible processes:

- (a) The direction of polarization of the domains may change. This would happen if all the  $\text{TiO}_6$  dipoles within a domain were to change their orientation, e.g. if all the dipoles in domain (ii) in Fig. 7.39 changed their orientation so as to be parallel to the dipoles in domain (i).
- (b) The magnitude of  $P$  within each domain may increase, especially if some randomness in dipole orientation is present before the field is applied.
- (c) *Domain wall* migration may occur such that favourably oriented domains grow in size at the expense of unfavourably oriented ones. For example, domain (i) in Fig. 7.39 may grow by migration of the domain wall one step to the right. To effect this, the dipoles at the edge of domain (ii) change their orientation to the positions shown dashed.

The ferroelectric state is usually a low-temperature condition since the effect of increasing thermal motions at high temperatures is sufficient to break down the common displacement in adjacent octahedra and destroy the domain structure. The temperature at which breakdown occurs is the ferroelectric Curie temperature,  $T_c$  (Table 7.3). Above  $T_c$ , the material is paraelectric (i.e. non-ferroelectric). High dielectric constants still occur above  $T_c$  (Fig. 7.40), but no residual polarization is retained in the absence of an applied field. Above  $T_c$   $\epsilon'$  is usually given by the Curie–Weiss Law,  $\epsilon' = C/(T - \theta)$ , where  $C$  is the Curie constant and  $\theta$  the Curie–Weiss temperature. Usually,  $T_c$  and  $\theta$  either coincide or differ by only a few degrees. The ferroelectric–paraelectric transition, at  $T_c$ , is an example of an order–disorder phase transition. However, unlike order–disorder phenomena in, say, brass, no long-range diffusion of ions occurs. Rather, the ordering that occurs below  $T_c$  involves preferential distortion or tilting of polyhedra and is therefore an example of a *displacive phase transition*. In the high temperature paraelectric phase, the distortions or tilts of the polyhedra, if they occur at all, are randomized.

A necessary condition for a crystal to exhibit spontaneous polarization and be ferroelectric is that its space group should be non-centrosymmetric. Often the symmetry of the paraelectric phase stable above  $T_c$  is centrosymmetric and the ordering transition that occurs on cooling simply involves a lowering of symmetry to that of a non-centric space group.

Several hundred ferroelectric materials are now known, including a large number of oxides that have distorted (non-cubic) perovskite structures. These contain cations that are happy in a distorted octahedral environment—Ti, Nb, Ta—and the asymmetric bonding within the  $\text{MO}_6$  octahedron gives rise to spontaneous polarization and a dipole moment. Not all perovskites are ferroelectric, e.g.  $\text{BaTiO}_3$  and  $\text{PbTiO}_3$  are whereas  $\text{CaTiO}_3$  is not, and this may be correlated with the ionic radii of the ions involved. It appears that the larger

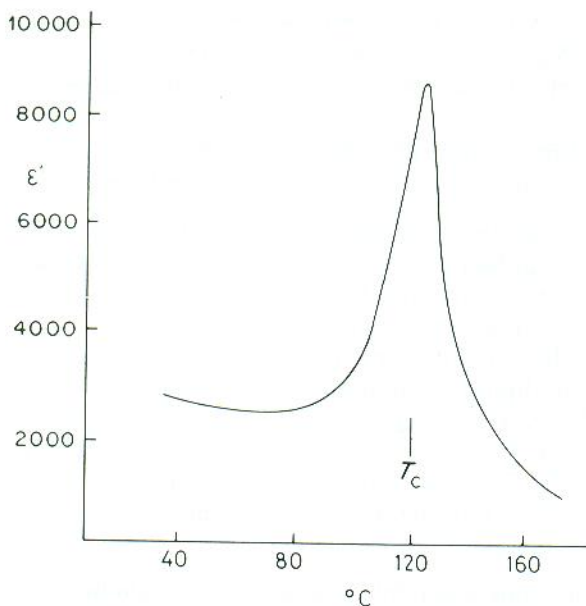


Fig. 7.40 Dielectric constant of barium titanate ceramic

$\text{Ba}^{2+}$  ion causes an expansion of the unit cell relative to  $\text{Ca}^{2+}$ ; this results in longer Ti—O bonds in  $\text{BaTiO}_3$  and allows the  $\text{Ti}^{4+}$  ions more flexibility to move within the  $\text{TiO}_6$  octahedra. Other ferroelectric oxides contain cations that are asymmetrically bonded because of the presence of a lone pair of electrons in their outer valence shell. These are the cations of the heavy *p*-block elements that are in oxidation states two less than the group valency, e.g.  $\text{Sn}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Bi}^{3+}$ , etc.

Ferroelectric oxides are used in capacitors because of their high dielectric constants, especially near to  $T_c$  (Fig. 7.40). In order to maximize  $\epsilon'$ , for practical applications, it is therefore necessary to displace the Curie point so that it is close to room temperature. The Curie point of  $\text{BaTiO}_3$ , 120°C (Fig. 7.40), may be lowered and broadened when either  $\text{Ba}^{2+}$  or  $\text{Ti}^{4+}$  are partially replaced by other ions. The substitution  $\text{Ba}^{2+} \rightleftharpoons \text{Sr}^{2+}$  causes a unit cell contraction and reduction in  $T_c$ ; replacement of 'active'  $\text{Ti}^{4+}$  by 'non-active' tetravalent ions such as  $\text{Zr}^{4+}$  and  $\text{Sn}^{4+}$  causes a rapid decrease in  $T_c$ .

A related type of spontaneous polarization occurs in *antiferroelectric* materials. In this, individual dipoles again occur but they generally arrange themselves so as to be antiparallel to adjacent dipoles (Fig. 7.38b). As a result, the net spontaneous polarization is zero. Above the antiferroelectric Curie temperature, the materials revert to normal paraelectric behaviour. Examples of antiferroelectrics, with their Curie temperatures, are: lead zirconate,  $\text{PbZrO}_3$ , 233°C; sodium niobate,  $\text{NaNbO}_3$ , 638°C; and ammonium dihydrogen phosphate,  $\text{NH}_4\text{H}_2\text{PO}_4$ , -125°C.

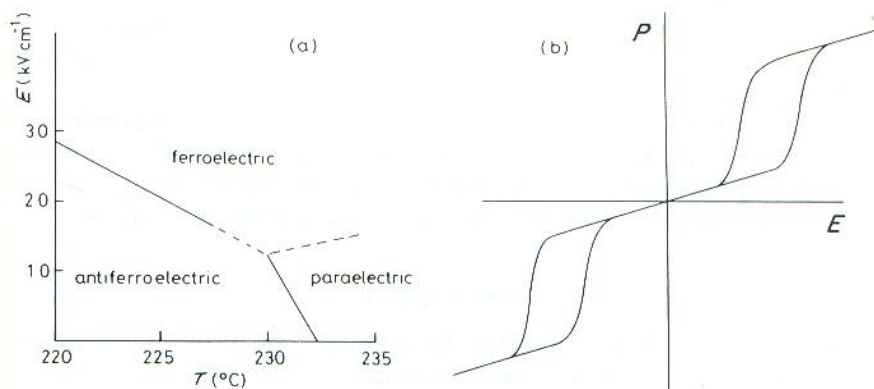


The electrical characteristics of antiferroelectrics are rather different to those of ferroelectrics. The antiferroelectric state is a non-polar one and no hysteresis loop occurs, although a large increase in permittivity may occur close to  $T_c$  (for  $\text{PbZrO}_3$ ,  $\epsilon' \simeq 100$  at  $200^\circ\text{C}$  and  $\simeq 3000$  at  $230^\circ\text{C}$ ). Sometimes, the antiparallel arrangement of dipoles in the antiferroelectric state is only marginally more stable than the parallel arrangement in the ferroelectric state and a small change in conditions may lead to a phase transition. For example, application of an electric field to  $\text{PbZrO}_3$  causes it to change from an antiferroelectric to a ferroelectric structure, Fig. 7.41(a); the magnitude of the field required depends on temperature. The polarization behaviour is then as shown in Fig. 7.41(b). At low fields, no hysteresis occurs and  $\text{PbZrO}_3$  is antiferroelectric; at high positive and negative fields, hysteresis loops occur and  $\text{PbZrO}_3$  is ferroelectric.

A related type of polarization phenomenon in which the structure is antiferroelectric in certain direction(s) only is shown in Fig. 7.38(c); in the  $x$  direction, the net polarization is zero and the structure is antiferroelectric, but in the  $z$  direction, a net spontaneous polarization occurs. This type of structure is known as *ferrielectric*; it occurs in, for example,  $\text{Bi}_4\text{Ti}_3\text{O}_{12}$  and lithium ammonium tartate monohydrate.

The importance of hydrogen bonding in certain ferroelectric and antiferroelectric materials is shown in Fig. 7.42. Ferroelectric  $\text{KH}_2\text{PO}_4$  and antiferroelectric  $\text{NH}_4\text{H}_2\text{PO}_4$  are both built of isolated  $\text{PO}_4$  tetrahedra that are linked together by  $\text{K}^+$  and  $\text{NH}_4^+$  ions and hydrogen bonds. These hydrogen bonds link up oxygens in adjacent  $\text{PO}_4$  tetrahedra. The two structures differ mainly in the position of hydrogen in the hydrogen bonds.

Each  $\text{PO}_4$  tetrahedron forms four hydrogen bonds with adjacent  $\text{PO}_4$  tetrahedra. In each of these hydrogen bonds, the hydrogens are displaced so as to be nearer to one oxygen or the other, i.e. in each hydrogen bond, the hydrogen atom has a choice of two positions, neither of which is midway along the bond.



**Fig. 7.41** (a) Antiferroelectric-ferroelectric transition in  $\text{PbZrO}_3$  as a function of the applied field,  $E$ . (b) Polarization behaviour across this transition



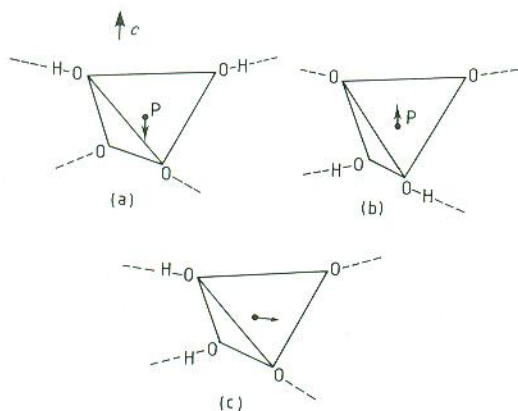


Fig. 7.42 Displacement of phosphorus within a  $\text{PO}_2(\text{OH})_2$  tetrahedron giving rise to spontaneous polarization

For each  $\text{PO}_4$  tetrahedron, therefore, two hydrogens are close and two are somewhat further away. In the high temperature, paraelectric forms of  $\text{KH}_2\text{PO}_4$  and  $\text{NH}_4\text{H}_2\text{PO}_4$ , the hydrogen positions are randomized over the two positions in each bond and a disordered structure obtains. In ferroelectric, low-temperature  $\text{KH}_2\text{PO}_4$ , the hydrogens order themselves so that both are associated with the upper edge of each  $\text{PO}_4$  tetrahedron (a). The hydrogens are responsible indirectly for spontaneous polarization within the  $\text{PO}_4$  tetrahedra since the phosphorus atoms are displaced downward away from the hydrogen atoms. This generates dipoles whose directions are parallel to the  $c$  crystallographic axis. In order to reverse the directions of the dipoles it is not necessary to bodily invert the tetrahedra. Instead, a simple movement of hydrogen atoms within the H bond achieves the same effect. The two hydrogens associated with the upper oxygens in (a) move away laterally to associate themselves with the lower oxygens of adjacent tetrahedra. At the same time, two hydrogens move in to associate themselves with the lower oxygens (b). This motion of hydrogen atoms *perpendicular* to  $c$  leads to dipole reversal *parallel* to  $c$ .

In antiferroelectric  $\text{NH}_4\text{H}_2\text{PO}_4$ , the two hydrogens of each tetrahedron are associated with one upper and one lower oxygen (c); this creates dipoles in a direction perpendicular to  $c$ . The dipole directions are reversed in adjacent tetrahedra and therefore, the net polarization over the whole crystal is zero.

### Pyroelectricity

Pyroelectric crystals are related to ferroelectric ones in that they are non-centrosymmetric and exhibit a net spontaneous polarization,  $P_s$ . Unlike ferroelectrics, however, the direction of  $P_s$  cannot be reversed by an applied electric field.  $P_s$  is usually temperature dependent:

$$\Delta P_s = \pi \Delta T \quad (7.22)$$