11

Insulating solids

- How are the relative permittivity and refractive index of a transparent solid related?
- What is the relationship between ferroelectric and pyroelectric crystals?
- How can a ferroelectric solid be made from a polycrystalline aggregate?

Solids have traditionally been divided into three classes when the electrical properties are described. Those that conduct electricity well are called conductors. This group is typified by metals. Those solids that conduct poorly are called semiconductors. This group contains elements such as silicon and germanium, and large numbers of minerals such as the iron sulphide fool's gold, FeS_2. Solids that do not conduct electricity are called insulators or dielectrics. Many oxides, such as magnesium oxide, MgO, and most polymers, such as polyethylene, are insulators.

This division is far too coarse to encompass the wide range of electrical properties that are now known. It is quite feasible to turn an insulating oxide into a very good 'metallic' conductor, and 'metallic' polymers are well known. However, all of the various possibilities can be understood in terms of the themes already presented – chemical bonding, crystal structure and microstructure. In this chapter the insulators are described. In Chapter 13 those materials that are conductors of electricity are discussed.

11.1 Dielectrics

11.1.1 Relative permittivity and polarisation

Insulators are explained in terms of chemical bonding as those solids in which the outer electrons are unable to move through the structure. They are localised in strong bonds if the material is considered to be a covalent compound, or else are restricted to the region close to an atomic nucleus if the compound is supposed to be ionic. In either case, these electrons are trapped and cannot move from one region to another.

Insulating materials are often referred to as dielectrics. One of the most important parameters used to describe an insulator is its dielectric constant, properly called the relative permittivity, ε_r.

Dielectrics form the working material in capacitors. A capacitor consisting of two parallel metal plates separated by a dielectric (including air) has a

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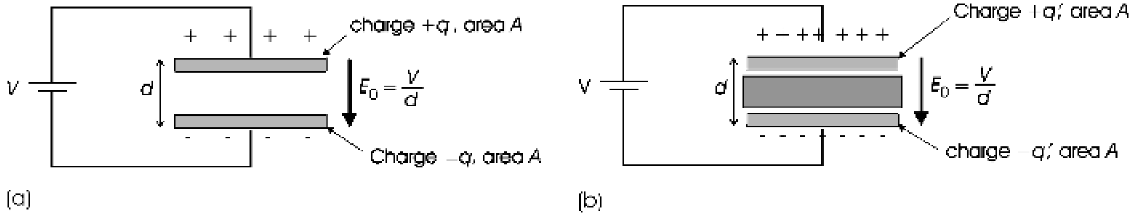


Figure 11.1 (a) Charges will accumulate on metal plates as a result of an applied voltage, V; the field between the plates, E_0, is equal to V/d. (b) A slab of dielectric (insulator) inserted between the plates will cause the charges on the plates to increase in proportion to its relative permittivity

capacitance, c, equal to the ratio of the charge on either of the metallic foils, q, to the potential difference, V, between them:

$$c = \frac{q}{V} \tag{11.1}$$

The relative permittivity of a material may be determined by making it a part of such a capacitor. If we arrange for two parallel metallic plates to be connected to a battery, a certain amount of charge will accumulate on the plates (Figure 11.1). In a vacuum (or air, in practice), we find

$$q = \frac{\varepsilon_0 A\, V}{d}$$

where q is the charge on the capacitor, ε_0 is a constant, the permittivity of free space, A is the area of the plates, and d their separation. A comparison with Equation (11.1) shows that the term $\varepsilon_0 A/d$ is the capacitance, c, of the device:

$$c = \frac{\varepsilon_0 A}{d}$$

If the region between the plates is now filled with a dielectric the charge and the capacitance increase by an amount ε_r:

$$q' = \frac{\varepsilon_0 \varepsilon_r A\, V}{d}$$

where ε_r is the relative permittivity of the material and has no units. The new capacitance, c', is:

$$c' = \frac{\varepsilon_0\, \varepsilon_r\, A}{d}$$

The relative permittivity describes the response of a solid to an electric field. The electric field is a vector quantity, ***E***, which has a direction pointing from positive to negative. When an insulating material is exposed to an external electric field, $\boldsymbol{E}_0$, arising from, for example, two charged metallic plates as in a capacitor, the negatively charged electrons and the positively charged nuclei will experience forces acting in opposite directions. The positive nuclei tend to move in the direction of the imposed electric field and the negative electrons in the opposite direction. The extent of this relative displacement will depend on how strongly the electrons are bound, the masses of the nuclei and the strength of the applied electric field. The displacement results in the formation of induced internal electric dipoles (Figure 11.2).

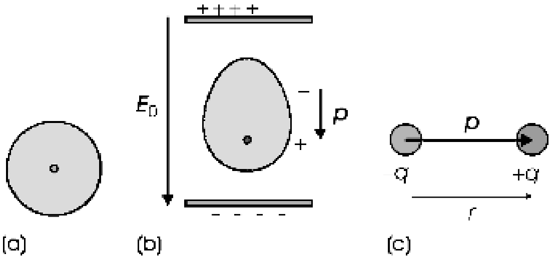


Figure 11.2 (a) For an atom in the absence of an electric field, the centres of gravity of the positive (nucleus) and negative (electrons) charges are coincident. (b) In an electric field these become separated to create a dipole. (c) An electric dipole consists of two equal and opposite charges separated by a distance r. The dipole moment is given by the vector ***p***, which points from negative to positive. The dipole gives rise to an electric field, ***E***, in the surrounding volume

Other constituents of the solid can also become polarised, and add to the effect, as described below.

Electric dipoles are vectors that run from the negative charge to the positive (Figure 11.2c). The magnitude of the dipole moment of a dipole, a vector $\boldsymbol{p}$, is defined as:

$$\boldsymbol{p} = q \times r$$

where q is the charge on the dipole, and r is the charge separation (see also Section S4.3). These induced dipoles add together with a result that opposite surfaces of the solid become positively and negatively charged (Figure 11.3). The solid becomes polarised. The polarisation of the dielectric, $\boldsymbol{P}$, is a vector quantity, defined as the electric dipole moment per unit volume. The polarisation vector, $\boldsymbol{P}$, points from the negative surface to the positive surface. In the case of a solid that is uniform in all directions (e.g. a glass or cubic crystal) it is found that at ordinary field strengths $\boldsymbol{P}$ is proportional and parallel to the applied electric field, $\boldsymbol{E}_0$, and we can write:

$$\boldsymbol{P} = \varepsilon_0\, \chi\, \boldsymbol{E}_0 \qquad (11.2)$$

where χ is called the dielectric susceptibility of the material, and ε_0 is the permittivity of free space. At higher electric field strengths, such as those found in laser beams, this relation can break down, and in this case it is better to replace the right-hand side of Equation (11.2) with a series, with $\varepsilon_0\, \chi\, \boldsymbol{E}$ as the first term (see Section 14.9.1). At normal field strengths, the electric susceptibility is related to the relative permittivity by the equation

$$\begin{aligned} \chi &= (\varepsilon_r - 1) \\ \boldsymbol{P} &= (\varepsilon_r - 1)\varepsilon_0\, \boldsymbol{E}_0 \end{aligned} \qquad (11.3)$$

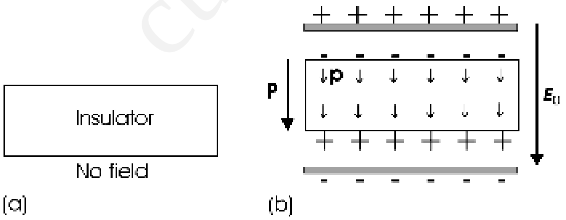


Figure 11.3 (a) In the absence of an applied electric field a dielectric has no surface charge. (b) In an electric field, $\boldsymbol{E}_0$, the material has a surface charge as a result of the formation of internal dipoles, $\boldsymbol{p}$, that induce an observable polarisation, $\boldsymbol{P}$

11.1.2 Polarisability

The bulk polarisation observed when a material is placed in an electric field is a result of the polarisability of the constituent parts of the solid, which can be the atoms, ions and so on that make up the solid. For ordinary electric field strengths, the electric dipole moment, $\boldsymbol{p}$, induced in a constituent, which might be an atom, for example, is proportional to the polarisability, α, of the constituent and the *local* electric field, $\boldsymbol{E}_{\text{loc}}$, acting on the constituent, thus:

$$\boldsymbol{p} = \alpha\, \boldsymbol{E}_{\text{loc}}$$

Note that the local field, $\boldsymbol{E}_{\text{loc}}$, is not the same as the applied field, $\boldsymbol{E}_0$, as it will include contributions from other dipoles present in the structure. Some of these may be permanent dipoles, but others will be temporary dipoles, induced by the applied electric field itself. When the dipole moment is in units of C m and the electric field strength is in V m^{-1}, the units of α are C m^2 V^{-1}. [These SI units are still rarely encountered in the literature, which mostly quotes values of the polarisability volume α', given in m^3, cm^3 or Å^3. See Section S4.3 for the conversion between the two units.] If there are N dipoles per unit volume:

$$\boldsymbol{P} = N\, \alpha\, \boldsymbol{E}_{\text{loc}} \qquad (11.4)$$

In principle, all constituents of a solid, including defects and internal surfaces, contribute to the polarisability. Thus, a solid with two components, A and B, containing 10 units of A and 15 units of B, of polarisability α_A and α_B, would have a polarisability:

$$\boldsymbol{P} = 10\boldsymbol{p}_A + 15\boldsymbol{p}_B = 10\, \alpha_A\, \boldsymbol{E}_{\text{loc}} + 15\, \alpha_B\, \boldsymbol{E}_{\text{loc}}$$

Similarly, if there are N_j types of constituent j of polarisability α_j, in a solid, the observed polarisation, $\boldsymbol{P}$, is:

$$\boldsymbol{P} = \sum_j N_j \boldsymbol{p}_j = \sum_j N_j \alpha_j \boldsymbol{E}_{\text{loc}}$$

where the local electric field acting on the constituent, $\boldsymbol{E}_{\text{loc}}$, may vary from site to site in the crystal. The most important sources of polarisation in insulating solids are derived from the atomic constituents that make up the material, as well as defects that may be present (Figure 11.4).

11.1.2.1 Electronic polarisability α_e

In the absence of an electric field, the electronic charge cloud surrounding an atom (at a little distance from the atom) is symmetrically disposed around the nucleus. In an electric field this charge cloud becomes deformed and the centre of the electronic negative charge is no longer coincident with the positive nuclear charge (Figure 11.4a), and a dipole will arise.

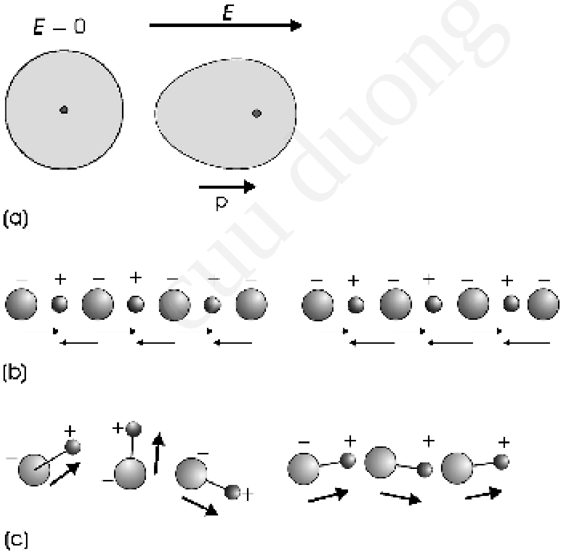


Figure 11.4 The effects of an electric field: (a) Electronic polarisation, (b) ionic polarisation and (c) orientational polarisation; dipoles are shown as arrows

11.1.2.2 Ionic polarisability α_i

Charged ions in a solid will suffer a displacement in an electric field. Similarly, the charge distribution in bonds between atoms can be altered by an electric field. This is illustrated for a linear chain of anions and cations in Figure 11.4(b).

11.1.2.3 Orientational polarisability α_d

A number of common molecules, including water, carry a permanent dipole. If such molecules are exposed to an electric field they will try to orient the dipole along the field (Figure 11.4c). As the movement of molecules in solids is restricted, orientational polarisability is more often noticed in gases and liquids.

11.1.2.4 Space charge polarisability α_s

If a material has mobile charges present they will move under the influence of the electric field, with positive charges moving towards one electrode and negative charges towards the other. These will tend to build up until the charge in the electrode regions, the space charge, inhibits further movement and equilibrium is reached. Good ionic conductors often show pronounced space charge effects.

11.1.2.5 Bulk polarisability α_{tot}

The observed bulk polarisability α_{tot} will arise from the sum of all the separate terms defined above. The total polarisability can be written as:

$$\alpha_{\text{tot}} = \alpha_{\text{e}} + \alpha_{\text{i}} + \alpha_{\text{d}} + \alpha_{\text{s}}$$

Note that other contributions can arise in some solids. In particular, if a solid contains a considerable number of defects these can make a significant contribution to the observed polarisation.

11.1.3 Polarisability and relative permittivity

To relate polarisability, α, to the relative permittivity, ε_{r}, it is necessary to remember that each constituent of the solid is polarised by a *local* electric field. This local field, $\boldsymbol{E}_{\text{loc}}$, is not the same as the applied field, $\boldsymbol{E}_0$, but will also include contributions from internal fields $\boldsymbol{E}_1$, $\boldsymbol{E}_2$, $\boldsymbol{E}_3$ and so on arising from the induced and permanent dipoles in the structure:

$$\boldsymbol{E}_{\text{loc}} = \boldsymbol{E}_0 + \boldsymbol{E}_1 + \boldsymbol{E}_2 + \boldsymbol{E}_3 + \cdots$$

Lorentz, using classical electrostatic theory, showed that the local field in an isotropic insulator such as a gas, a glass or a crystal with cubic symmetry is uniform everywhere and given by:

$$\boldsymbol{E}_{\text{loc}} = \boldsymbol{E}_0 + \frac{\boldsymbol{P}}{3\,\varepsilon_0} \tag{11.5}$$

Using Equations (11.3)–(11.5) it is possible to derive the most widely used relationship between relative permittivity and polarisability, the Clausius–Mossotti relation, Equation (11.6), usually written:

$$\frac{\varepsilon_{\text{r}} - 1}{\varepsilon_{\text{r}} + 2} = \frac{N\,\alpha}{3\,\varepsilon_0} \tag{11.6}$$

where α is the polarisability of the material, and N is the number of atoms or formula units of structure per unit volume. If there are j types of atom or structural unit, all with differing polarisabilities, the sum of $N_j\,\alpha_j$ is needed. Remember that this equation is applicable only to homogeneous isotropic materials that do not contain permanent dipoles or dipolar molecules. In fact, this means that its use is restricted to glasses, amorphous solids and cubic crystals that show only electronic and ionic polarisability. However, it is often taken to be approximately true for crystals of lower symmetry, provided that they do not contain permanent dipolar molecules.

Several alternative forms of the Clausius–Mossotti equation are encountered. Frequently, the term N is replaced by its reciprocal, the volume of one atom or one formula unit of structure, $V_{\text{m}} = 1/N$ and is set out in terms of α, thus:

$$\alpha = 3\,\varepsilon_0\,V_{\text{m}}\frac{\varepsilon_{\text{r}} - 1}{\varepsilon_{\text{r}} + 2} \tag{11.7}$$

Quite often, the equation is expressed in terms of the molar polarisability, $\boldsymbol{P}_{\text{m}}$. This form is obtained by multiplying both sides of Equation (11.6) by M/ρ, where M is the molar mass of the material and ρ is its density, to obtain:

$$\frac{(\varepsilon_{\text{r}} - 1)M}{(\varepsilon_{\text{r}} + 2)\rho} = \frac{N_{\text{A}}\,\alpha}{3\,\varepsilon_0} = \boldsymbol{P}_{\text{m}}, \tag{11.8}$$

where $\boldsymbol{P}_{\text{m}} = N_{\text{A}}\,\alpha/3\,\varepsilon_0$ and N_{A} is the Avagadro constant, given by MN/ρ.

As mentioned in Section 11.1.2, the literature mainly quotes the polarisability volume, α', rather than the SI polarisability, α. In this case, the common form of the Clausius–Mossotti equation encountered is:

$$\alpha' = \left(\frac{3\,V_{\text{m}}}{4\,\pi}\right)\left(\frac{\varepsilon_{\text{r}} - 1}{\varepsilon_{\text{r}} + 2}\right) \tag{11.9}$$

where V_{m} is the volume of one formula unit of structure. The units of α' will be the same as those of V_{m}.

11.1.4 The frequency dependence of polarisability and relative permittivity

As the total polarisability of a material, α, is made up several contributions, the relative permittivity, ε_{r}, can also be thought of as made up from the same contributions. In a static electric field, all the various contributions will be important, and both α and ε_{r} will arise from electrons, ions, dipoles, defects and surfaces. However, if a variable, especially alternating, electric field acts on the solid the situation changes.

At low enough frequencies the value of the relative permittivity measured will be identical to the static value, and all polarisability terms will contribute to ε_{r}. However, space charge polarisation is usually unable to follow changes in electric field that occur much faster than that of radio frequencies, about 10^6 Hz, and this contribution will no longer be registered at frequencies higher than this value. Similarly, any dipoles present are usually unable to rotate to and fro in time with the alternations of the electric field when frequencies reach the microwave region, about 10^9 Hz, and at higher

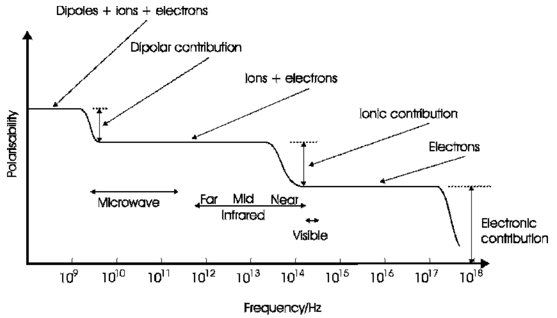


Figure 11.5 The contribution of electronic, dipole, ionic and orientation polarisability to the overall polarisability of a solid

frequencies this contribution will be lost. Ionic polarisability, involving the movement of atomic nuclei, is no longer registered when the frequency of the field approaches that of the infrared range, 10^{12} Hz. Electrons, being the lightest components of matter, still respond to an alternating electric field at frequencies corresponding to the visible region, 10^{14} Hz, but even the contribution of electronic polarisability ‘drops out’ at ultraviolet frequencies (Figure 11.5).

The interaction of an alternating electric field with a solid in the frequency range between the infrared and ultraviolet – the optical range – is more commonly expressed as the refractive index, because a lightwave consists of oscillating electric and magnetic fields. The relative permittivity in the optical region is related to the refractive index n by:

$$n^2 = \varepsilon_r \tag{11.10}$$

This relationship as such is not well obeyed for most compounds if the static or low-frequency relative permittivity is used, as can be judged from Table 11.1. The relationship can be correctly interpreted by using the relative permittivity due to electronic polarisation in the equation. With this in mind, substitution of the relationship given in Equation (11.10) into the Clausius–Mossotti equation yields the Lorentz–Lorenz equation:

$$\frac{n^2 - 1}{n^2 + 2} = \frac{N\,\alpha_e}{3\,\varepsilon_0} \tag{11.11}$$

The to-and-fro interaction of the components of a solid with an alternating electric field dissipates energy and results in heating of the dielectric. It also causes a lag between the phase of the input field and the phase of the output field. The action of an alternating electric field in best described by using the complex dielectric constant

$$\varepsilon_r = \varepsilon_0(\varepsilon' - \mathrm{i}\,\varepsilon'')$$

Table 11.1 The relative permittivity and refractive index of some crystals

Compound	Symmetry	Relative permittivity, ε_r	Frequency Hz	Refractive index, n	n^2
Diamond	Cubic	5.66	10^3	2.418	5.85
Periclase, MgO	Cubic	9.65	10^2–10^8	1.735	3.010
Spinel, $MgAl_2O_4$	Cubic	8.6	–	1.719	2.955
Fluorite, CaF_2	Cubic	6.81	10^2–10^{11}	1.434	2.056
Corundum, Al_2O_3	Hexagonal		10^2–10^9		
perpendicular to c		9.34		1.761	3.101
along c		11.54		1.769	3.129
Beryl, $Be_3Al_2Si_6O_{18}$	Hexagonal		10^3		
perpendicular to c		6.86		1.589	2.525
along c		5.95		1.582	2.503
Rutile TiO_2	Tetragonal		10^4–10^6		
along a and b		86		2.609	6.807
along c		170		2.900	8.410

where $\mathrm{i} = \sqrt{-1}$. The loss tangent, $\tan\delta$, then specifies the phase lag, where:

$$\tan\delta = \frac{\varepsilon''}{\varepsilon'}$$

The loss tangent is a measure of the energy loss in a capacitor. For good dielectrics, $\tan\delta$ is about 10^{-4} and is relatively insensitive to the frequency of the applied field.

11.1.5 Polarisation in nonisotropic crystals

In the preceding discussion it has not, strictly speaking, been necessary to regard the electric field and polarisation as vectors. However, in most crystalline solids the direction of an applied electric field is unlikely to be parallel to the induced polarisation. When the shapes of groups of atoms in a crystal are considered it is reasonable to think that polarisation will be easier in some directions than in others. To treat this it is usual to define a set of orthogonal axes in the crystal and refer the applied electric field to these axes. These axes are conveniently taken to coincide with the crystallographic axes for tetragonal and orthorhombic systems. In hexagonal systems one axis is taken to coincide with the crystallographic *c* axis, and the other two are normal to the *c* axis. In monoclinic and triclinic crystals it is still possible to define three Cartesian axes, although the relationship between these and the crystallographic axes is not so simple.

The relative permittivity (as well as the refractive index) for such crystals is quoted as three values corresponding to the polarisations projected onto the axes. Some representative values are given in Table 11.1.

It may sometimes be necessary to estimate the polarisability of a solid in the absence of experimental data. Polarisability is not particularly easy to measure, but the relative permittivity is. The Clausius–Mossotti equation, Equation (11.6), is generally used to obtain polarisability from relative permittivity. The equation gives reasonable values for isotropic solids showing only ionic and electronic polarisation. If the refractive index is known, the Lorentz–Lorentz equation, Equation (11.11), will yield the electronic polarisability of the material. Hence, by difference, the ionic polarisability can be estimated.

In the absence of relative permittivity data for the solid under consideration it is possible to make use of the additivity rule. In its simplest form, we can write:

$$\alpha(\text{compound}) = \sum \alpha(\text{components})$$

For example, for an oxide mineral:

$$\alpha(\text{mineral}) = \Sigma\,\alpha(\text{component oxides})$$
$$\alpha(\mathrm{Mg_2SiO_4}) = 2\,\alpha(\mathrm{MgO}) + \alpha(\mathrm{SiO_2})$$

A more extended form of the additivity rule is obtained if the ‘components’ are actual ions or atoms. In the example above, we would then write:

$$\alpha(\mathrm{Mg_2SiO_4}) = 2\,\alpha(\mathrm{Mg^{2+}}) + \alpha(\mathrm{Si^{4+}}) + 4\,\alpha(\mathrm{O^{2-}})$$

11.2 Piezoelectrics, pyroelectrics and ferroelectrics

11.2.1 The piezoelectric and pyroelectric effects

In a normal dielectric, the observed polarisation of the material is zero in the absence of an electric field, and this does not change if the material is heated or subjected to mechanical deformation. In a piezoelectric solid a surface electric charge develops when the solid is subjected to a mechanical stress such as pressure, even in the absence of an external electric field. This is called the direct piezoelectric effect. The effect is reversible and the inverse (or converse) piezoelectric effect, in which a voltage applied to a crystal causes a change in shape, also occurs in piezoelectric crystals. The piezoelectric effect generally varies from one direction to another in a crystal, and in some directions a crystal may show no piezoelectric effect at all whereas in other directions it is pronounced.

Piezoelectric solids are a subset of dielectrics. All piezoelectrics are dielectrics, but only some dielectrics are piezoelectrics.

In the case of a pyroelectric solid a change of temperature induces a polarisation change. The change in polarisation found on heating is reversed on cooling. Pyroelectric crystals are a subset of piezoelectrics. All pyroelectric crystals are piezoelectrics, but not all piezoelectrics demonstrate pyroelectricity. A material that is a pyroelectric is found to possess a spontaneous polarisation, $\boldsymbol{P}_s$. This means that a pyroelectric crystal shows a permanent polarisation that is present both in the absence of an electric field and in the absence of mechanical stress.

The relative permittivity values normally encountered in crystals are rather small (Table 11.1). Some crystals, however, exhibit relative permittivity values many orders of magnitude higher than those in normal dielectrics. For example, one crystallographic polymorph of barium titanate, $BaTiO_3$, has a relative permittivity, ε_r, of the order of 20 000 (more values are given in Table 11.2.). By analogy to magnetic behaviour, this behaviour is called ferroelectricity, and the materials are called ferroelectrics. Ferroelectrics also possess a spontaneous polarisation, $\boldsymbol{P}_s$, in the absence of an electric field and a mechanical distortion. They are, therefore, a subset of pyroelectrics and, as such, all ferroelectrics are also pyroelectrics and piezoelectrics. The feature that distinguishes ferroelectrics from pyroelectrics is that the direction of the spontaneus polarisation, $\boldsymbol{P}_s$, can be switched (changed) in an applied electric field, as described below.

The hierarchy of insulating properties can be summarised thus (Figure 11.6):

- If polarisation, $\boldsymbol{P}$, changes with applied electric field, $\boldsymbol{E}$, we have a dielectric.

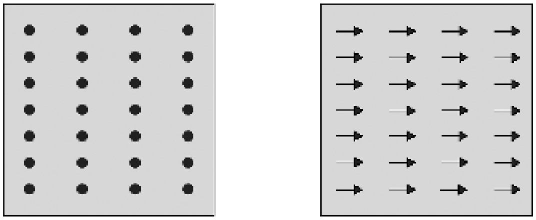
- In some dielectrics the polarisation, $\boldsymbol{P}$, can arise from mechanical stress, σ, to give a piezoelectric.

- In some piezoelectrics, there is a spontaneous polarisation, $\boldsymbol{P}_s$, when the applied electric field,

Table 11.2 Ferroelectrics and antiferroelectrics

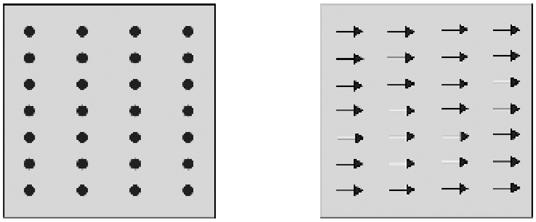
Compound	Formula	T_C/K	$\boldsymbol{P}_s$/C m^{-2}	Approximate ε_r
Hydrogen-bonded compounds:				
Rochelle salt	$NaK(COO \cdot CHOH)_2 \cdot 4\,H_2O$	298	0.01	5×10^3
Triglycine sulphate	$(NH_2CH_2COOH)_3 \cdot H_2SO_4$	322	0.03	2×10^3
Potassium dihydrogen sulphate	KH_2PO_4	123	0.05	6×10^5
Polar groups:				
Sodium nitrite	$NaNO_2$	436	0.08	1.1×10^3
Perovskites:				
Barium titanate	$BaTiO_3$	403	0.26	1×10^4
Lead titanate	$PbTiO_3$	763	0.80	9×10^3
Potassium niobate	$KNbO_3$	691	0.30	4.5×10^3
Tungsten bronzes:				
Sodium barium niobate	$Ba_2NaNb_5O_{15}$	833	0.40	6×10^4
Antiferroelectrics:				
Tungsten trioxide	WO_3	1010	0	300*
Ammonium dihydrogen phosphate	$NH_4H_2PO_4$	148	0	57, 10*
Lead hafnate	$PbHfO_3$	476	0	200*
Lead zirconate	$PbZrO_3$	503	0	150*
Sodium niobate	$NaNbO_3$	627	0	700, 70*

*Varies with crystal direction. Upper and lower values are given when these differ substantially.
Note: T_C, Curie temperature; $\boldsymbol{P}_s$, spontaneous polarisation; ε_r, relative permittivity.



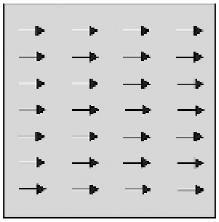
(i) $\boldsymbol{E} = 0$ (ii) $\boldsymbol{E}$ is finite

(a) Dielectric

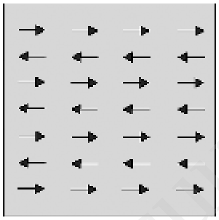


(i) $\sigma = 0$ (ii) σ is finite

(b) Piezoelectric



(c) Pyroelectric and ferroelectric, $\boldsymbol{E}$ – 0, σ – 0



(d) Antiferroelectric: $\boldsymbol{E}$ – 0, σ – 0

Figure 11.6 Schematic relationship between dielectric solids ($\boldsymbol{E}$ is an applied electric field, and σ is an applied stress). (a) Dielectric: (i) $\boldsymbol{E} = 0$, (ii) $\boldsymbol{E}$ is finite; a dielectric, normally unpolarised, becomes polarised is an electric field). (b) Piezoelectric: (i) $\sigma = 0$, (ii) σ is finite; (a piezoelectric, normally unpolarised, developes a polarisation when subjected to stress, even is no electric field). (c) Pyroelectric and ferroelectric: $\boldsymbol{E} = 0$, $\sigma = 0$. (d) Antiferroelectric: $\boldsymbol{E} = 0$, $\sigma = 0$ (pyroelectric, ferroelectric and antiferroelectric solids contain dipoles when both electric field and stress are zero)

E, and the stress, σ, are zero, which changes with temperature, T, to give pyroelectrics.

- In some pyroelectrics the spontaneous polarisation, $\boldsymbol{P}_s$, is easily switched in an electric field, to give a ferroelectric.

11.2.2 Piezoelectric mechanisms

A piezoelectric crystal develops surface charges as a result of bulk polarisation due to the formation of internal dipoles or to the rearrangement of existing dipoles. To give an idea of how polarisation can be produced on the application of pressure, two examples are described below.

11.2.2.1 Example 1: metal–oxygen tetrahedra

In the first example, suppose that a crystal is built up of metal–oxygen MO_4 tetrahedra. (Note: piezoelectricity is not confined solely to crystals containing tetrahedral groups.) In an ideal MO_4 tetrahedron the centre of gravity of the negative charges, arising from the combined effects of the oxygen atoms and the chemical bonds, will coincide with the centre of gravity of the positive charges arising in the metal atom, M (Figure 11.7a). A force applied to the top of a tetrahedron will cause a deformation. The oxygen–metal bond in line with the force will resist deformation most, as the positive metal and negative oxygen atoms are being forced together. The basal triangle of oxygen atoms will be flattened and as there are no metal atoms to oppose this change directly, it will occur to a greater degree than will the other deformation. The centre of gravity of the negative charges will no longer coincide with the centre of gravity of the positive charge, and a dipole will result.

The direction of the force is important and in some directions stress will not cause polarisation to occur. A force directed perpendicular to a tetrahedron edge (Figure 11.7b) will deform all bonds equally, and not give rise to any dipoles.

When this idea is applied to a crystal, the results for all the tetrahedra need to be added together. If

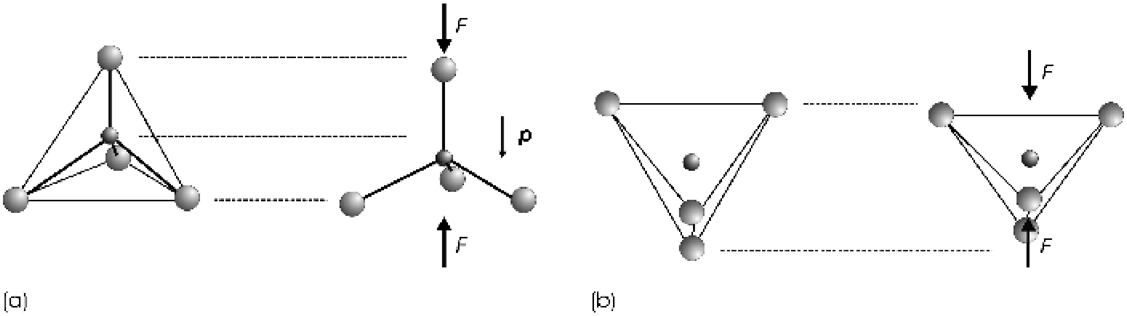


Figure 11.7 (a) A load, F, applied to a tetrahedron along a bond gives rise to a dipole as a result of distortion. (b) A load, F, applied perpendicular to a tetrahedron edge does not

the unit cell in the crystal has a centre of symmetry the overall polarisation of adjacent tetrahedra must add to zero. If the structure lacks a centre of symmetry the dipoles will add to give the unit cell an overall dipole moment. In this case an external polarisation will appear. Thus, piezoelectric materials are characterised by a lack of a centre of symmetry. In fact, there are 21 crystal classes that lack a centre of symmetry and, of these, 20 are piezoelectric classes.

11.2.2.2 Example 2: dipole-containing crystals

The piezoelectric effect can also be generated in a crystal already containing dipoles. In some materials the elementary dipoles add to zero in the absence of stress. When the crystal is deformed the dipole directions rotate slightly, so that an overall polarisation is observed. This happens in quartz, SiO_2, one of the best-known piezoelectric solids. Although frequently drawn in a idealised form, with regular [SiO_4] tetrahedra (Figure 11.8a), at room temperature the tetrahedra are considerably distorted, and each gives rise to a small permanent dipole (Figure 11.8b). In the unstressed structure these cancel, to give no net polarisation. When stress is applied, the tetrahedra distort slightly (Figure 11.8c), with a consequence that the dipoles no longer cancel and an overall polarisation is produced.

In the case of crystals showing spontaneous polarisation, the elementary dipoles are already

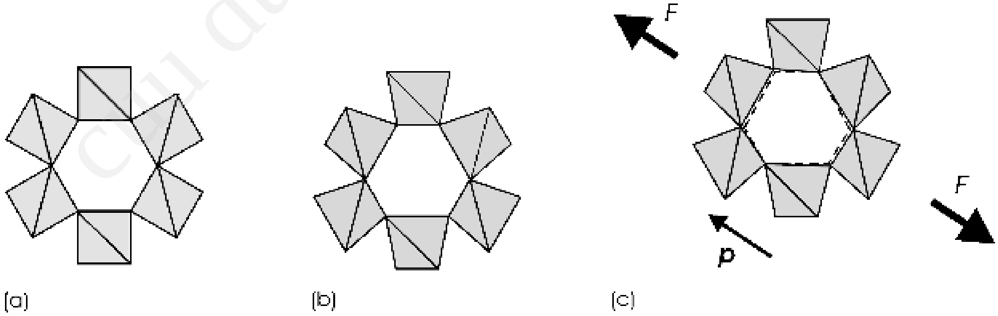


Figure 11.8 (a) Part of the idealised structure of high-temperature (β) quartz drawn as corner-connected [SiO_4] tetrahedra, projected down the c axis (note that the tetrahedra are arranged in a helix, not in rings). (b) Part of the structure of room-temperature (α) quartz; the tetrahedra are distorted and each gives rise to an electric dipole, but these add to zero in the unit shown and over a unit cell. (c) Application of a load, F, to the structure in the direction drawn distorts the structure from the unstressed form, shown as dotted lines, so that the dipoles no longer cancel. This leads to the overall dipole, $\boldsymbol{p}$. Similar diagrams can be drawn for other directions; not all give rise to observable dipoles

ordered. In this case the application of stress will cause a change in the relative dispositions of the dipoles. This will lead to a change in the observed polarisation. In these solids the piezoelectric effect is a measurement of the change in polarisation that has accompanied the stress.

The requirement that the piezoelectric effect is restricted to noncentrosymmetric crystals implies that piezoelectricity should not be observed in a polycrystalline solid. This is because the individual grains will polarise in random directions that will cancel overall. It is possible to get around this problem in some piezoelectric materials, as described in Section 11.3.8.

11.2.3 Piezoelectric polymers

At first sight it might seem surprising that polymers can exhibit piezoelectricity, but it is so. Indeed, the requirements to produce piezoelectricity are the same as those just given. That is, the material should contain pressure-induced or pressure-sensitive elementary dipoles, and these should be incorporated into a crystalline matrix that lacks a centre of symmetry. Piezoelectric polymers generally rely on permanent dipoles on the polymer chains. There are two main sources of these dipoles in polymers: strongly polar bonds such as carbon–fluorine (C–F), carbon–chlorine (C–Cl), carbon–nitrogen (C–N) and hydrogen bonds. Polar carbon–fluorine bonds are found in polymers such as poly(vinyl fluoride), $[\mathrm{CH_2{-}CHF}]_n$, known as PVF (Figure 11.9a), and poly(vinylidene fluoride), $[\mathrm{CH_2{-}CF_2}]_n$, known as $\mathrm{PVF_2}$ (Figure 11.9b). The negative end of the dipole is located on the fluorine atom, $\mathrm{C} \leftarrow \mathrm{F}$, and a smaller dipole is found on the carbon–hydrogen bond, $\mathrm{C} \rightarrow \mathrm{H}$ (Figure 11.9a.i). In PVF, the overall dipole moment is greatest in the isotactic form of the polymer, in which all of the fluorine atoms are on the same side of the carbon–carbon backbone (Figure 11.9a.ii). As would be expected, atactic polymers, in which the fluorine atoms have a random distribution do not show a significant piezoelectric effect. The polymer $\mathrm{PVF_2}$ also has an overall dipole composed of two $\mathrm{C} \leftarrow \mathrm{F}$ dipoles (Figure 11.9b.i) opposed by two $\mathrm{C} \rightarrow \mathrm{H}$ dipoles. The isotactic form of the polymer (Figure 11.9b.ii) has the highest net dipole moment. Defects in the chain, especially caused by irregular linking of the monomer units during polymerisation, reduce the overall dipole moment of the chains.

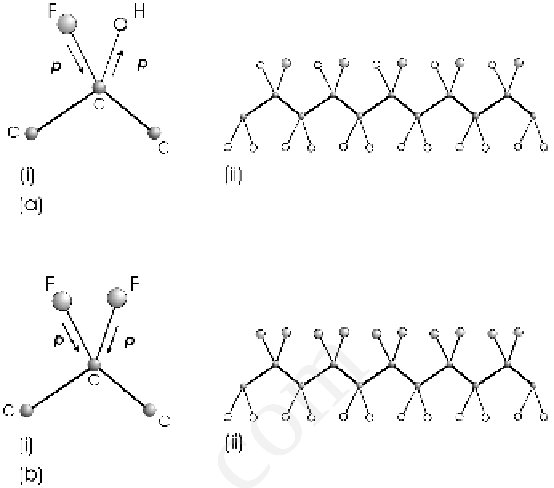


Figure 11.9 (a) Poly(vinyl fluoride), PVF, $[\mathrm{CH_2{-}CHF}]_n$: (i) dipoles present in a tetrahedral unit of PVF and (ii) isotactic structure of a polymer chain of PVF. (b) Poly(vinylidene fluoride), $\mathrm{PVF_2}$, $[\mathrm{CH_2{-}CF_2}]_n$: (i) dipoles present in a tetrahedral unit of $\mathrm{PVF_2}$ and (ii) isotactic structure of a polymer chain of $\mathrm{PVF_2}$

Hydrogen bonding produces the polarisation in polyamides, better known as nylons. The relative configurations of the hydrogen-bond dipoles depend on the spacing between the amide groups along the polymer chain (Figure 11.10). In the case of even polymers, such as nylon 6 (Figure 11.10a), dipoles are opposed along the chain. In odd polymers, such as nylon 5 (Figure 11.10b), the dipoles are aligned to give an observable polarisation.

In addition to the presence of elementary dipoles, it is important for the polymer to crystallise or partly crystallise into noncentrosymmetric structures. The polymer chains can usually pack together in several different ways. For example, poly(vinylidene fluoride), $\mathrm{PVF_2}$, can crystallise in four forms. The arrangement of the chains in one nonpolar and one polar form is drawn schematically in Figure 11.11. Naturally, the degree of crystallinity of the

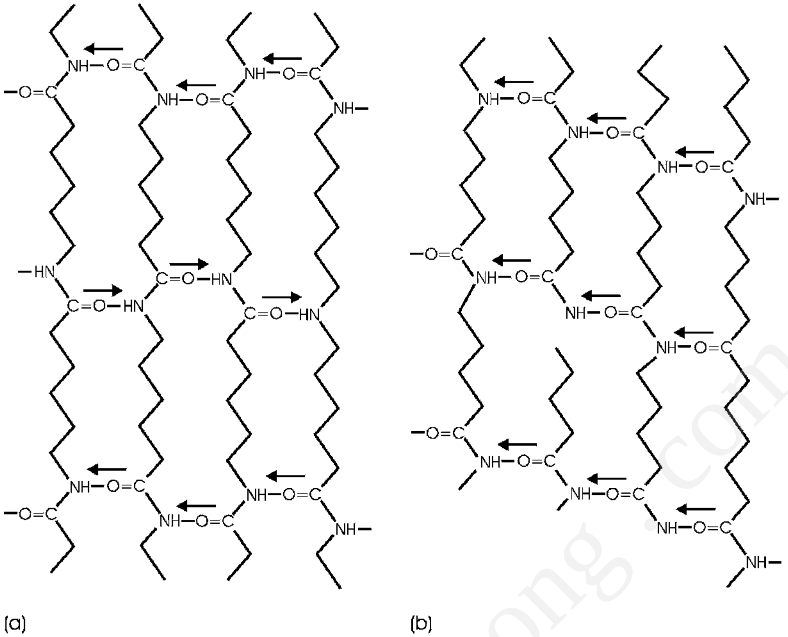


Figure 11.10 (a) The electric dipoles present in chains of an even nylon, nylon 6; no overall dipole moment is observed. (b) The electric dipoles present in chains of an odd nylon, nylon 5; the dipoles add to produce an observed dipole moment

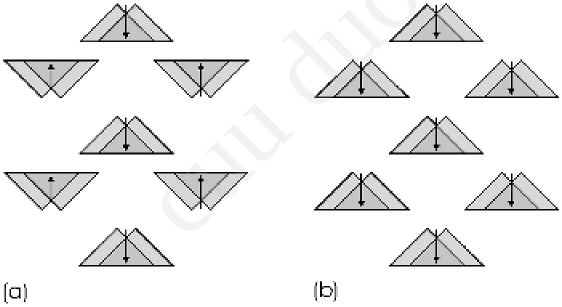


Figure 11.11 The schematic crystal structure of two forms of poly(vinylidene fluoride), PVF_2, viewed down the polymer chains, shown as double triangles; the electric dipoles in the chains are drawn as arrows. (a) The dipoles cancel in a centrosymmetric structure and the material is a nonpiezoelectric. (b) The dipoles add together in a noncentrosymmetric structure and the material is piezoelectric

polymer strongly influences the magnitude of the observed piezoelectric effect. Careful processing is important in the production of good piezoelectric films.

Piezoelectric plastic sheets can also be fabricated. These materials are known as electrets. Electrets are thin polymer films of high resistance that are polarised in a high field or by having an electric charge 'sprayed' onto the surface from a discharge. The resistance is so high that they retain the polarisation so induced permanently. In these materials, the dipole moment is very large, because of the large separation (in atomic terms) of the charges on the opposed faces of the plastic.

Although polymer piezoelectrics do not generally have as high piezoelectric coefficients as ceramic materials, they have some important advantages. Among other things, polymer films are of low density and are flexible, which makes them suitable for use in sensors and transducers in microphones, keyboards and flat-panel speakers.

11.2.4 The pyroelectric effect

As noted briefly in Section 11.2.1, a pyroelectric crystal possesses a spontaneous polarisation, $\boldsymbol{P}_s$. The polarisation is a result of elementary dipoles in the crystal that are aligned to give an observable external bulk polarisation at all times (Figure 11.6c). Despite this, it is a matter of common observation that a pyroelectric crystal does not usually show an external charge. This is because the surface charges are neutralised by ions or other charged particles picked up from the air. Nevertheless, when a pyroelectric crystal is heated or cooled the spontaneous polarisation will change as a result of the thermal expansion of the solid, but the collection of neutralising particles will take time to arrive, and a pyroelectric effect will be seen. Pyroelectric crystals kept clean and in a vacuum maintain their surface charges for many days.

The relationship between the change in spontaneous polarisation, $\Delta \boldsymbol{P}_s$ and the change in temperature, ΔT, can be written as:

$$(\Delta \boldsymbol{P}_s)_i = \pi_i \, \Delta T$$

where π_i is the pyroelectric coefficient, with units of $\mathrm{C\,m^{-2}\,K^{-1}}$, and i takes values of 1, 2 or 3 and refers to the (unique) x, y or z axis. Typical values of π are of the order of $10^{-5}\,\mathrm{C\,m^{-2}\,K^{-1}}$.

As in the case of piezoelectrics, the elementary dipoles will cancel out if the crystallographic unit cell has a centre of symmetry. However, another condition is also needed to produce a spontaneous polarisation, the presence of a unique polar axis, which is a direction in the crystal unrelated by symmetry to any other direction, not even the antiparallel direction. The dipoles lie parallel to the polar axis of the crystal (see Section 5.1.3). Of the 20 piezoelectric crystal classes, only 10 fulfil this criterion and give rise to the pyroelectric effect. The relationship between the appearance of piezoelectricity and pyroelectricity and the symmetry of the crystal is set out in Figure 11.12.

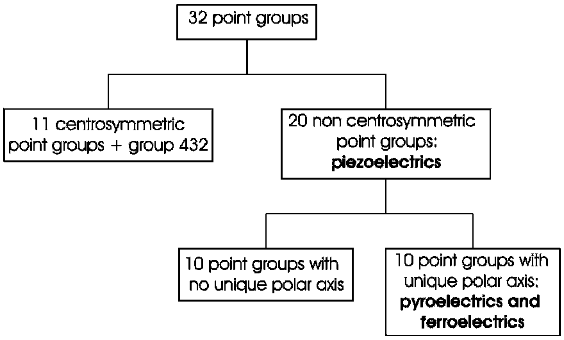


Figure 11.12 The relationship between point group and piezoelectric and pyroelectric properties

The pyroelectric effect that is normally observed in a crystal is, in fact, composed of two separate effects called the primary (or true) pyroelectric effect and the secondary pyroelectric effect. If a crystal is fixed so that its size is constant as the temperature changes, the primary effect is measured. Normally, though, a crystal is unconstrained. An additional pyroelectric effect will now be measured, the secondary pyroelectric effect, caused by strains in the crystal produced by the thermal change. In general, the secondary effect is much greater than the primary effect, but both are utilised in devices.

Among the structurally simplest pyroelectrics are hexagonal ZnO (zincite) and the isostructural hexagonal ZnS (wurtzite). In these crystals, the structure is built of layers of metal and nonmetal atoms, with the metals surrounded by a tetrahedron of nonmetals (Figure 11.13). The tetrahedra are

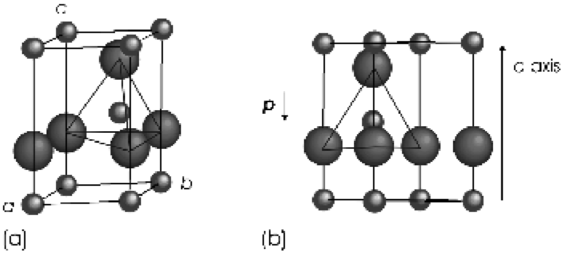


Figure 11.13 (a) The structure of hexagonal ZnO (zincite); a ZnO_4 tetrahedron is outlined. (b) An electric dipole, $\boldsymbol{p}$, parallel to the c axis, arises in the unsymmetrical ZnO_4 tetrahedron; the wurtzite form of ZnS is isostructural

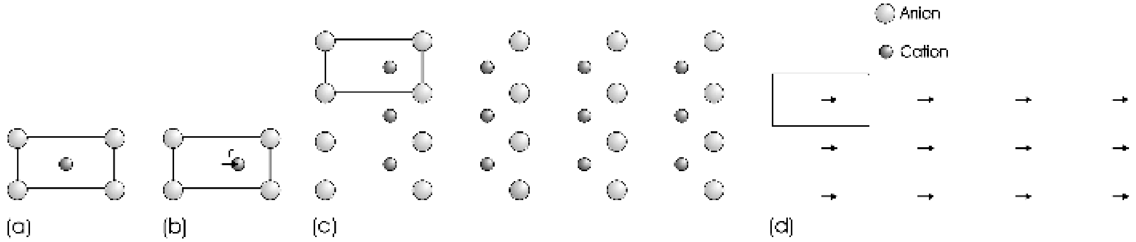


Figure 11.14 (a) A cation-centred unit cell; (b) cation displacement, *r*, creating an electric dipole in each cell; (c) an array of unit cells; and (d) an array of electric dipoles

slightly flattened, which gives rise to an electric dipole lying parallel to the polar axis, the *c* axis. Materials showing the pyroelectric effect are used as infrared radiation detectors.

11.3 Ferroelectrics

11.3.1 Ferroelectric crystals

Ferroelectrics are distinguished from pyroelectrics by virtue of the fact that the spontaneous polarisation, $\boldsymbol{P}_s$, can be switched in direction. A variety of crystallographic features can result in ferroelectric behaviour, and many different chemical compounds are classified as ferroelectrics. Some details are given below for three important classes of ferroelectrics – those involving hydrogen bonds, those involving polar groups and those involving medium-sized transition-metal cations.

Because of this wide variation, it is preferable to explain the process by way of a simple model. Suppose we have a rectangular array of anions and that the structure gains stability when the cations are displaced slightly from the centre of the surrounding anion coordination polyhedron (i.e. if the cations are placed as illustrated in Figure 11.14b rather than as in Figure 11.14a). (This frequently happens for relatively small cations.) The centre of gravity of the anion array will not now coincide with the positive cation, and each 'rectangle' in the structure now contains a dipole (Figure 11.14c). Repetition of this motif results in an aligned dipole array characteristic of a ferroelectric (Figure 11.14d).

The cation displacement can take place in one of two directions. A plot of the potential energy of the cation against position will have two minima, separated by a potential energy barrier, ΔU, corresponding to the two alternative displacements (Figure 11.15). During crystallisation a cation in a crystal nucleus might occupy either of these positions at random. Thereafter, local interactions tend to make cations in adjoining 'rectangles' line up so as to form a parallel set of dipoles. Crystal nuclei in different parts of the crystal will take any of the two possible orientations. As growth continues the crystallites ultimately touch and the crystal contains domains of differing polarisation. For example, in Figure 11.14(d) the cation displacement could also occur in the opposite direction to that drawn, resulting in the domain boundary shown in

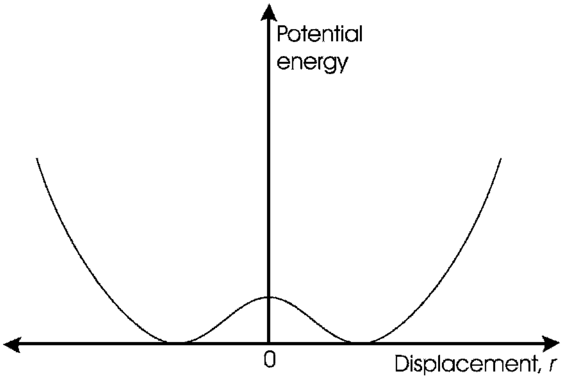


Figure 11.15 The variation of potential energy with cation displacement, ±*r*, from the centre of a surrounding anion polyhedron

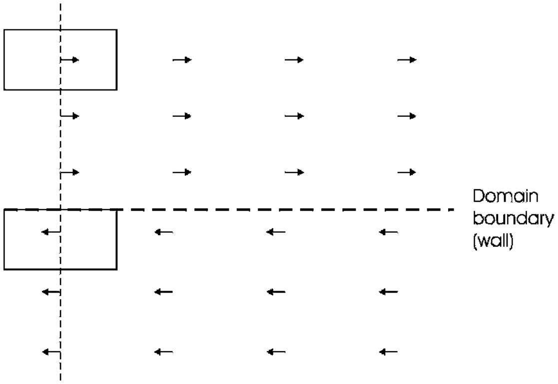


Figure 11.16 Domains due to the differing alignment of dipoles in adjacent regions of a crystal. The regions are separated by a domain wall, which extends over several tens of nanometres in practice

Figure 11.16. The number of different domains that are found in an actual crystal will depend on the number of different displacement directions that are possible. This is generally greater than two, and domain structures can be complicated. In general, crystals that exhibit a domain structure are called ferroic materials.

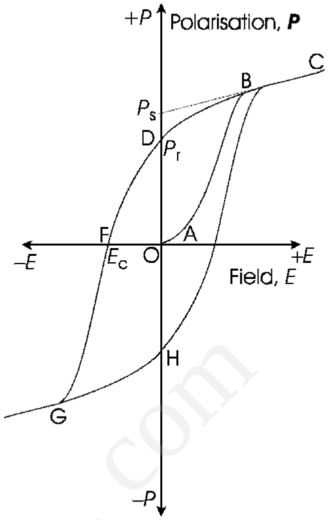


Figure 11.17 Hysteresis behaviour of the polarisation, ***P***, in relation to the applied electric field, ***E***, for a ferromagnetic crystal. As the field takes values between $+E$ and $-E$, the polarisation, P, takes values between $+P$ and $-P$

11.3.2 Hysteresis in ferroelectric crystals

In general, a ferroelectric crystal will be composed of an equal number of domains oriented in all the equivalent directions allowed by the crystal symmetry. The overall polarisation of the crystal will be zero. If we now apply a small electric field, ***E***, in a nominally positive direction, the crystal will behave like a normal dielectric, as the value of ***E*** is not great enough to overcome the energy barrier ΔU (Figure 11.15). In Figure 11.17 this corresponds to the segment O–A. As ***E*** increases, cations will start to gain sufficient energy to overcome the energy barrier and will be able jump from one potential well to the other. The elementary dipole direction will switch. Gradually, all of the domains will change orientation and the observed polarisation will now increase rapidly, corresponding to section A–B of Figure 11.17. Ultimately, all of the dipoles will be aligned parallel and the crystal will, in principle, consist of a single domain. This is the state of saturation, B–C (Figure 11.17). On reducing and then reversing the applied electric field the converse takes place. Gradually, dipoles switch direction, following path C–D–F–G, to reach saturation, with dipoles pointing in the opposite direction, at G (Figure 11.17). Reversal of the electric field again causes a reversal of dipole direction, and the curve will follow the path G–H–C. This closed circuit is called a hysteresis loop. The value OD is called the remanent polarisation, $\boldsymbol{P}_{\mathrm{r}}$, and OF is called the coercive field, $\boldsymbol{E}_{\mathrm{C}}$. Extrapolation of the linear portion of the curve, B–C, to $E = 0$ gives the value of the spontaneous polarisation $\boldsymbol{P}_{\mathrm{S}}$. The most important characteristic of a ferroelectric is that the spontaneous polarisation can be reversed by the application of a suitably oriented electric field.

11.3.3 Antiferroelectrics

Ferroelectricity is governed by two types of factors: (a) chemical bonds, which are short-range forces, and (b) dipolar interactions, which are long-range forces (Section 3.1.1). Calculations of the energy of ferroelectric crystals indicate that a minimum energy results when all the elementary dipoles are parallel or all the dipoles are in an antiparallel arrangement (Figure 11.6). The antiparallel arrangement is found in antiferroelectrics. Dielectric measurements are needed to establish the antiferroelectric behaviour of a material.

The balance between ferroelectric and antiferroelectric states is delicately poised, and some antiferroelectrics readily transform to ferroelectric states. This transformation is often accompanied by a change in the crystal structure of the solid. For example, orthorhombic lead zirconate, $PbZrO_3$, which is antiferroelectric, can transform to rhombohedral lead zirconate, $PbZrO_3$, which is ferroelectric. In the system $PbZrO_3$–$PbTiO_3$, as the smaller Ti^{4+} ion replaces the larger Zr^{4+} ion, the antiferroelectric phase is replaced by a ferroelectric state. Some ferroelectrics and antiferroelectrics are listed in Table 11.2.

11.3.4 The temperature dependence of ferroelectricity and antiferroelectricity

The fact that an applied field can cause the polarisation to alter its direction implies that the atoms involved make only small movements and that the energy barrier between the different states is low. With increasing temperature the thermal motion of the atoms will increase, and eventually they can overcome the energy barrier separating the various orientations. Thus at high temperatures the distribution of atoms becomes statistical and the crystal behaves as a normal dielectric and no longer as a polar material. This is referred to as the paraelectric state. The temperature at which this occurs is known as the Curie temperature, T_c, or the transition temperature. The relative permittivity often rises to a sharp peak in the neighbourhood of T_c.

The temperature dependence of the relative permittivity of many ferroelectric crystals in the paraelectric state can be described fairly accurately by a relationship called the Curie–Weiss law:

$$\varepsilon_r = \frac{C}{T - T_c} \qquad (11.12)$$

where ε_r is the relative permittivity, C is a constant, T_c is the Curie temperature, and T is the absolute temperature. The value of the constant, C, is determined by a plot of $1/\varepsilon_r$ versus T:

$$\frac{1}{\varepsilon_r} = \frac{T}{C} - \frac{T_c}{C}$$

Ideally the graph is linear, with a slope of $1/C$ and an intercept on the T axis of T_c (Figure 11.18). Frequently, the point of intercept, T_0, is slightly different from the measured value of T_c, and the Curie–Weiss equation is often written in the form

$$\varepsilon_r = \frac{C}{T - T_0}$$

where T_0 is the extrapolated Curie temperature (Figure 11.18).

11.3.5 Ferroelectricity due to hydrogen bonds

Hydrogen bonds are formed when a hydrogen atom sits between two electronegative atoms in an off-centre position (Section 3.1.1). At temperatures below the Curie temperature the hydrogen atoms

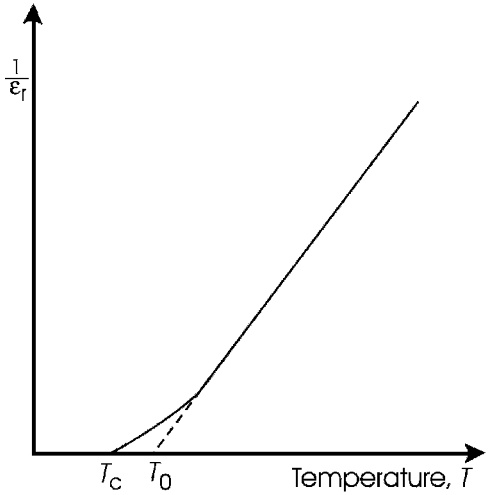


Figure 11.18 The Curie–Weiss behaviour of a ferroelectric solid above the Curie temperature T_c. Note: ε_r, relative permittivity; T, absolute temperature

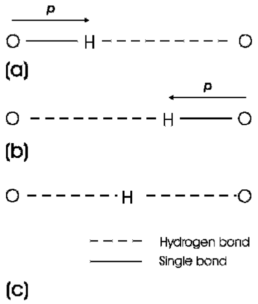


Figure 11.19 (a) and (b) Below the ferroelectric transition temperature, T_c, hydrogen atoms in hydrogen bonds lie to one side or the other of the centre. (c) Above T_c the hydrogen atoms are, on average, central. Hydrogen bonds are shown as broken lines, and normal covalent bonds are shown as continuous lines

are ordered on one side of the hydrogen bond or the other (Figure 11.19a). As the hydrogen in a hydrogen bond can occupy two equally stable positions, it is not difficult to see a possible origin for the switching. A sufficiently high electric field will swap the dipole direction by causing the hydrogen ion to jump to the alternative position (Figure 11.19b). At temperatures higher than the Curie temperature, atomic vibrations induced by thermal energy overcome the barrier between the two alternative positions and the hydrogen atoms will occupy an average position between the two adjacent electronegative atoms (Figure 11.19c). The polar nature of the solid is lost. The compounds in this group are ordered at lower temperatures and become disordered at higher temperatures. This type of change is called an order–disorder transition.

Hydrogen bonding is the origin of ferroelectricity in potassium dihydrogen phosphate (KH_2PO_4), Rochelle salt [sodium potassium tartrate; $Na(COO.\text{-}CHOH \cdot CHOH \cdot COO)K \cdot 4H_2O$] and triglycine sulphate [$(NH_2CH_2COOH)_3 \cdot H_2SO_4$]. However, the interaction of the hydrogen bonds with other features of the crystal structure usually makes each compound unique, and the dipoles giving rise to ferroelectricity may lie in other parts of the structure.

This feature is well illustrated by the transition in KH_2PO_4. At a temperature above 123 K KH_2PO_4 is paraelectric. The skeleton of the structure (Figure 11.20a) is made up of regular (PO_4) tetrahedra connected by hydrogen bonds (broken lines in Figure 11.20a). On average, the hydrogen atoms are found at the centres of the hydrogen bonds. The low-temperature form of KH_2PO_4 exists below 123 K. In this structure, the hydrogen atoms (shown as black circles) order (Figure 11.20b) so that each (PO_4) tetrahedron in the high-temperature form is converted into a [$PO_2(OH)_2$] tetrahedron.

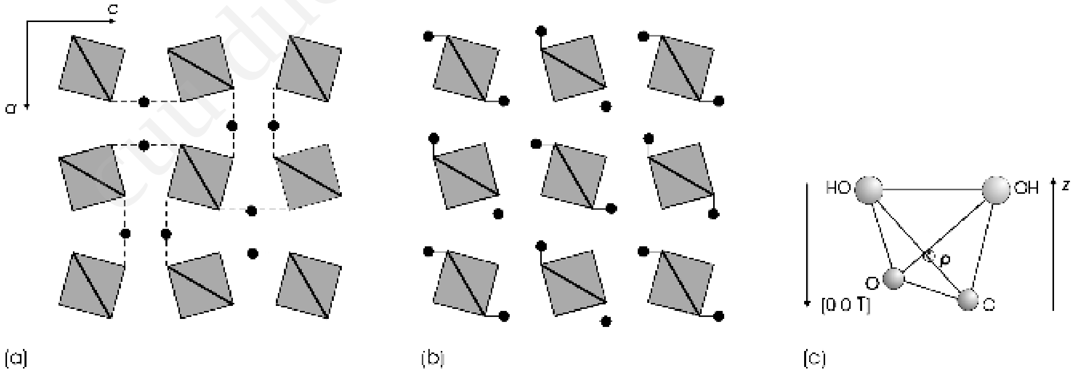


Figure 11.20 Potassium dihydrogen phosphate, KH_2PO_4: (a) skeleton of the structure of KH_2PO_4 projected down the [0 0 1] direction (the PO_4 tetrahedra are shown in projection as squares; the hydrogen bonds are shown as broken lines; the potassium atoms are omitted); (b) low-temperature structure showing ordered H atoms (black circles). (c) The displacement of the P atoms in the PO_4 tetrahedra as a result of the H-atom ordering, and the subsequent formation of (OH) groups, induces an electric dipole, ***p***, parallel to the *c* axis

The phosphorus atoms in the tetrahedra are off-centre, pushed away by the hydrogen atoms. The dipoles responsible for ferroelectricity arise in these tetrahedra. They lie along the $[0\,0\,\bar{1}]$ direction and the z axis is the polar axis. The O—H···O bonds are almost perpendicular to these dipoles, and, although hydrogen bonding is the prime cause of ferroelectricity, the hydrogen bonds themselves are not the seat of the dipoles. However, the off-centre positions of the phosphorous and hydrogen atoms are closely linked. When an external field is applied the hydrogen and the phosphorous atoms switch in concert.

Ammonium dihydrogen phosphate, $NH_4H_2PO_{4,}$ is structurally and chemically very similar to the ferroelectric KH_4PO_4, but the proton ordering is different, and $NH_4H_2PO_4$ is an antiferroelectric below the transition temperature.

11.3.6 Ferroelectricity due to polar groups

Compounds with dipolar groups such as $(NO_3)^-$, which is pyramidal, and nitrite, $(NO_2)^-$, which is shaped like an arrowhead, can also produce ferrroelectric phases. At temperatures below the Curie temperature these angular units are locked into one position in the solid in an ordered array. In cases where the geometry of the crystal structure will allow, a sufficiently high electric field can reorient such groups, thus causing the dipole to point in a different direction. At temperatures above the Curie temperature these groups disorder, and ferroelectric behaviour is lost. The compounds in these two groups are ordered at lower temperatures and become disordered at higher temperatures. This type of change is an order–disorder transition.

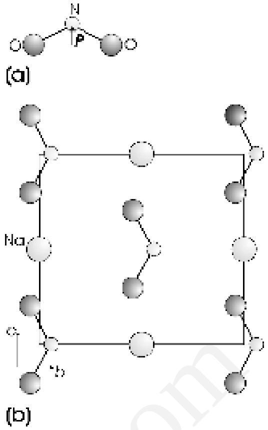


Figure 11.21 (a) The structure of a planar nitrite, (NO_2^-) group; the electric dipole, $\boldsymbol{p}$, in each unit points towards the nitrogen (N) atom. (b) The low-temperature structure of sodium nitrite, $NaNO_2$, projected down the $[1\,0\,0]$ direction; the dipoles are aligned along the b axis. In the high-temperature paraelectric form the dipoles are arranged at random along $+b$ and $-b$

As an example, consider sodium nitrite, $NaNO_2$. The structure is similar to that of halite, NaCl, and, if the NO_2 groups were spherical instead of shaped like blunt arrowheads, it would be identical (Figure 11.21). These groups point along the b axis with their planes perpendicular to the a axis. As each NO_2 group is polar, the structure is polar, with the dipoles pointing along the b axis. In an applied electric field the NO_2 groups can be made to reverse, and the material is a ferroelectric. There are two ways in which the dipoles could change direction. The nitrogen atom could flip between the oxygen atoms, but this does not occur, as the NO_2 ion is fairly rigid. Instead, the NO_2 groups rotate in their own plane.

The ferroelectric-to-paraelectric phase transition occurs at 165 °C, and in the paraelectric phase the net dipole moment has been lost. Although this could be due to free rotation of the NO_2 groups, this, in fact, does not happen. In reality, the high-temperature structure is disordered. Half of the NO_2 dipoles point along $+b$ and half point along $-b$. This transition is an order–disorder transition and its onset is gradual. At 150 °C, 15 °C below the transition temperature, some 10 % of the NO_2 groups have reversed their orientation.

11.3.7 Ferroelectricity due to medium-sized transition-metal cations

Ferroelectric properties can be attributed to the presence of medium-sized cations in many oxides with structures related to that of perovskite, for example $BaTiO_3$ and $KNbO_3$. These contain ions such as Ti^{4+} and Nb^{5+}, surrounded by six O^{2-} ions in an octahedral geometry. At lower temperatures, these cations are usually displaced from the centre of the surrounding oxygen coordination polyhedron. These ions can jump from one off-centre position to another under the influence of an electric field. Above the Curie temperature the ions occupy an average position in the coordination polyhedron, and a net dipole is lost. This type of transformation is a displacive transition.

As an example, consider barium titanate, $BaTiO_3$. Above 120 °C the paraelectric form of $BaTiO_3$ has the cubic perovskite structure, with $a_0 = 0.4018$ nm (Figure 11.22a). The large Ba^{2+} cations are surrounded by 12 oxygen ions, and the medium-sized Ti^{4+} ions are situated at the centre of an octahedron of oxygen ions. Below 120 °C the phase becomes ferroelectric. Between 120 °C and above 5 °C the unit cell is tetragonal (Figure 11.22b), with $a_0 = 0.3997$ nm, and $c_0 = 0.4031$ nm. (There are other structures with lower symmetries found at temperatures below 5 °C that will not be considered here.) As the crystal cools through the cubic–tetragonal transition temperature, the cubic cell expands slightly along one edge to produce the tetragonal c axis and is slightly compressed along the other two edges to form the tetragonal a and b-axes. The change from cubic to tetragonal is accompanied by an off-centre movement of the octahedrally coordinated Ti^{4+} ions, accompanied by a slight change in octahedron dimensions. This results in the formation of a dipole pointing along the c axis (Figure 11.22c). The change in the Ba^{2+} positions is almost negligible. The polar axis is the c axis. The off-centre Ti^{4+} position in an octahedron can be changed in an electric field and hence tetragonal $BaTiO_3$ is a ferroelectric.

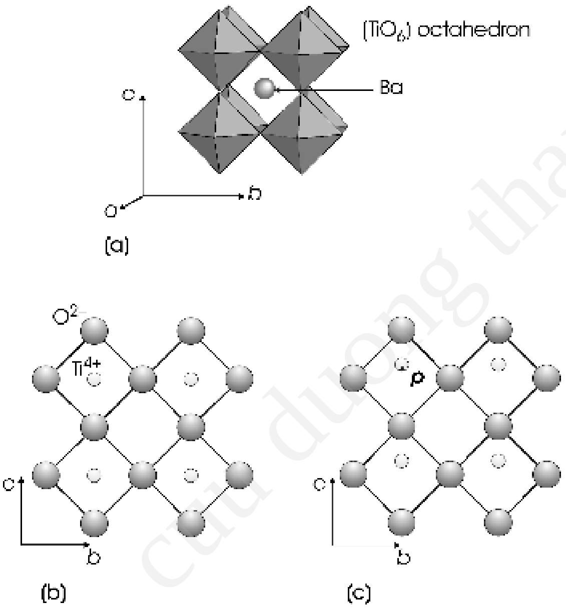


Figure 11.22 (a) The cubic perovskite structure of high-temperature cubic barium titanate, $BaTiO_3$, drawn as corner-shared TiO_6 octahedra; the Ba^{2+} ions occupy the unit cell centre. (b) Projection of the structure down the [1 0 0] direction, with the Ba^{2+} ions omitted. (c) Schematic view of the low-temperature tetragonal form, with the displacements of the Ti^{4+} ions exaggerated and the Ba^{2+} ions omitted. The electric dipoles, $\boldsymbol{p}$, generated by the off-centre displacement of the Ti^{4+} ions, point along the c axis of the tetragonal unit cell

There is no preference as to which of the original cubic axes becomes the polar direction, and so this can take one of six equivalent directions, parallel to $\pm x$, $\pm y$ or $\pm z$. On cooling, a ferroelectric domain pattern forms, reflecting that the transformation takes place along any of the allowed cubic directions in various parts of the phase.

11.3.8 Poling and polycrystalline ferroelectric solids

A ferroelectric crystal does not normally show any observable polarisation, because the domain structure leads to overall cancellation of the effect. Polycrystalline ceramics would be expected to be similar. In order to form a material with an observable polarisation the crystals are poled. This process involves heating the crystals above the Curie point, T_c, and then cooling them in a strong electric field. The effect of this is to favourably orient dipoles so that the crystal or polycrystalline ceramic shows a strong ferroelectric effect. The majority of ferroelectric materials used are, in fact, polycrystalline.

The same is true of polymer piezoelectrics. In these materials, the crystallites that give rise to piezoelectricity are oriented at random within the polymer matrix. Poling can give the dipoles an overall preferred orientation. Naturally, poling will not affect a crystallite that does not show a permanent dipole, and so poling applies only to pyroelectric and ferroelectric materials.

11.3.9 Doping and modification of properties

Many ferroelectric materials show interesting and potentially useful properties, but not at the temperature or pressure required for a particular application. It is then necessary to change or 'tune' the property to the fit the application. This change is frequently brought about by the replacement of one or more of the constituents of the compound, or the deliberate addition of impurities. As in the case of semiconductors and other materials, the deliberate addition of impurities to change the physical properties of a solid is known as doping.

Ferroelectric oxides, for example, are of interest as capacitor materials because of their high permittivity levels, but usually the sharp maximum in dielectric constant at the Curie point must be broadened and moved to room temperature. Consider $BaTiO_3$, which has a high dielectric constant at the Curie temperature, about 393 K. The Curie temperature can be increased by the replacement of some of the Ba^{2+} ions by Pb^{2+} ions. These ions are 'softer' (i.e. more easily polarised) than the Ba^{2+} ions, as they have a lone pair of electrons and so are more easily affected by an applied electric field. The resultant compound retains the crystal structure of $BaTiO_3$ but has a formula $Ba_{1-x}Pb_xTiO_3$. The compound $Ba_{0.6}Pb_{0.4}TiO_3$ has a Curie temperature of approximately 573 K, an increase of 200 K. In a similar way, the Curie temperature can be lowered by the substitution of Ba^{2+} ions by Sr^{2+}. These ions are smaller than Ba^{2+} ions and can be considered to be 'harder' and more difficult to polarise. The compound $Ba_{0.6}Sr_{0.4}TiO_3$ has a Curie temperature of 0 °C. The Curie temperature can also be lowered by the replacement of some of the Ti^{4+} ions by Zr^{4+} or Sn^{4+} ions. In this type of doping, the normal ferroelectric behaviour, due to off-centre Ti^{4+} ions in TiO_6 octahedra, is simply modified.

Answers to introductory questions

How are the relative permittivity and refractive index of a transparent solid related?

The observed bulk polarisability of a solid, α, will arise from the sum of a number of separate terms such as electronic polarisability, ionic polarisability and so on. As the total polarisability of a material is made up several contributions, the relative permittivity, ε_r, can also be thought of as made up from the same contributions. In a static electric field, all the various contributions will be important and both α and ε_r will arise from electrons, ions, dipoles, defects and surfaces.

An alternating electric field acts on these components in different ways. At low frequencies the value of the relative permittivity measured will be identical to the static value, and all polarisability terms will contribute to ε_r. However, space charge polarisation is usually unable to follow changes in electric field that occur much faster than that of radio frequencies, about 10^6 Hz, and this contribution will no longer be registered at frequencies higher than this value. Similarly, any dipoles present are usually unable to rotate to and fro in time with the alternations of the electric field when frequencies reach the microwave region, about 10^9 Hz, and at higher frequencies this contribution will be lost. Ionic polarisability, involving the movement of atomic nuclei, is no longer registered when the frequency of the field approaches that of the infrared range, 10^{12} Hz. Electrons, being the lightest components of matter, still respond to an alternating electric field at frequencies corresponding to the visible region, 10^{14} Hz.

The interaction of an alternating electric field with the electrons in a solid in the frequency range between the infrared and ultraviolet–the optical range–is more commonly expressed as the refractive index, because a lightwave consists of oscillating electric and magnetic fields. The relative permittivity in the optical region is related to the refractive index by:

$$n^2 = \varepsilon_r$$

What is the relationship between ferroelectric and pyroelectric crystals?

In a piezoelectric solid a surface electric charge develops when the solid is subjected to a mechanical stress such as pressure, even in the absence of an external electric field. This is called the piezoelectric effect, and crystals that exhibit this behaviour are called piezoelectrics. Piezoelectric solids are a subset of dielectrics. All piezoelectrics are dielectrics, but only some dielectrics are piezoelectrics.

In the case of a pyroelectric solid a change of temperature induces a polarisation change. Pyroelectric crystals are a subset of piezoelectrics. All pyroelectric crystals are piezoelectrics, but not all piezoelectrics demonstrate pyroelectricity. A material that is a pyroelectric is found to possess a spontaneous polarisation, $\boldsymbol{P}_s$. This means that a pyroelectric crystal shows a permanent polarisation that is present both in the absence of an electric field and in the absence of mechanical stress.

Some crystals, however, exhibit relative permittivity values many orders of magnitude higher than found in normal dielectrics. By analogy with magnetic behaviour, this behaviour is called ferroelectricity, and the materials are called ferroelectrics. Ferroelectrics also possess a spontaneous polarisation, $\boldsymbol{P}_s$, in the absence of an electric field and a mechanical distortion. They are, therefore, a subset of pyroelectrics and, as such, all ferroelectrics are also pyroelectrics and piezoelectrics. The feature that distinguishes ferroelectrics from pyroelectrics is that the direction of the spontaneous polarisation, $\boldsymbol{P}_s$, can be switched (changed) in an applied electric field.

How can a ferroelectric solid be made from a polycrystalline aggregate?

A ferroelectric crystal does not normally show any observable polarisation because the domain structure leads to overall cancellation of the effect. Polycrystalline ceramics would be expected to be similar. In order to form a material with an observable polarisation the crystals are poled. This process involves heating the crystals above the Curie point, T_c, and then cooling them in a strong electric field. The effect of this is to favourably orient dipoles so that the crystal or polycrystalline ceramic shows a strong ferroelectric effect. The majority of ferroelectric materials used are, in fact, polycrystalline.

The same is true of polymer piezoelectrics. In these materials, the crystallites that give rise to piezoelectricity are oriented at random within the polymer matrix. Poling can give the dipoles an overall preferred orientation. Naturally, poling will not affect a crystallite that does not show a permanent dipole, and so poling applies only to pyroelectric and ferroelectric materials.

Further reading

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Problems and exercises

Quick quiz

1 The relative permittivity of a material is also called the:
  (a) Dielectric constant
  (b) Dielectric permittivity
  (c) Dielectric susceptibility

2 The polarisation of a solid in an electric field is due to:
  (a) The formation of charges on the surface
  (b) The flow of charges from one surface to the other
  (c) The formation of electric dipoles

3 The dielectric susceptibility relates the:
  (a) Polarisation of a solid to the charges in a solid
  (b) Polarisation to the capacitance of a solid
  (c) Polarisation of a solid to the electric field

4 The polarisability is *not* a property of:
  (a) Surfaces
  (b) Atoms
  (c) Ions

5 One of the following will *not* contribute to the polarisability of a nonmolecular solid in a static electric field:
  (a) Ionic polarisability
  (b) Orientational polarisability
  (c) Electronic polarisability

6 Which of the following contributes to the polarisability of a solid in a very-high-frequency electric field:
  (a) Ionic polarisability?
  (b) Electronic polarisability?
  (c) Space charge polarisability?

7 The relative permittivity of a crystal with cubic symmetry is:
  (a) The same in all directions
  (b) Different along each crystallographic axis
  (c) Different along two out of the three axes

8 The relative permittivity of a crystal with hexagonal symmetry is:
  (a) The same in all directions
  (b) The same along the *a* and *b* axes, and different along the *c* axis
  (c) Different along the *a*, *b* and *c* axes

9 The relative permittivity of a crystal with tetragonal symmetry is:
  (a) The same along the *a*, *b* and *c* axes
  (b) The same along the *a* and *b* axes, and different along the *c* axis
  (c) Different along the *a*, *b* and *c* axes

10 The relative permittivity of a crystal with orthorhombic symmetry is:
  (a) The same along the *a*, *b* and *c* axes
  (b) The same along the *a* and *b* axes, and different along the *c* axis
  (c) Different along the *a*, *b* and *c* axes

11 In the direct piezoelectric effect:
  (a) An applied voltage causes a dimensional change
  (b) A dimensional change produces a voltage
  (c) An applied voltage produces a temperature change

12 A spontaneous polarisation is *not* found in:
  (a) Piezoelectric solids
  (b) Ferroelectric solids
  (c) Pyroelectric solids

13 A solid that has a switchable spontaneous polarisation is:
  (a) A pyroelectric
  (b) A piezoelectric
  (c) A ferroelectric

14 A piezoelectric must contain:
  (a) Tetrahedral groups
  (b) Octahedral groups
  (c) No centre of symmetry

15 For a polymer to be potentially piezoelectric it needs:
(a) An amorphous structure
(b) Permanent dipoles
(c) A crystalline structure

16 Electrets are:
(a) Polymer sheets with a permanent surface charge
(b) Polymer sheets with permanent internal dipoles
(c) Polymer sheets that are charged easily

17 The crystal structure of pyroelectric crystals must contain:
(a) A polar axis
(b) A centre of symmetry
(c) Switchable permanent dipoles

18 Ferroelectric crystals must posses:
(a) Hydrogen bonds
(b) Switchable dipoles
(c) Polar groups

19 Ferroics are solids that contain:
(a) Domain structures
(b) Ferroelectric domains
(c) Magnetic domains and ferroelectric domains

20 Hysteresis is characteristic of:
(a) Pyroelectric crystals
(b) Piezoelectric crystals
(c) Ferroelectric crystals

21 The dipoles in an antiferroelectric crystal are:
(a) In parallel rows
(b) In antiparallel rows
(c) Partly aligned

22 The paraelectric state of a ferroelectric is:
(a) The high-temperature phase
(b) The low-temperature phase
(c) The antiferroelectric phase

23 The Curie temperature is *not* the temperature at which:
(a) A ferroelectric transforms to a paraelectric state
(b) A paraelectric transforms to a ferroelectric state
(c) A ferroelectric transforms to an antiferroelectric state

24 The temperature dependence of the relative permittivity of many ferroelectric crystals obeys the Curie–Weiss Law:
(a) In the ferroelectric state
(b) In the paraelectric state
(c) At low temperatures

25 Hydrogen bonding is *not* the cause of ferroelectricity in:
(a) Triglycine sulphate
(b) Rochelle salt
(c) Sodium nitrite

26 The cause of ferroelectricity in perovskite materials is often due to:
(a) The presence of medium-sized cations in octahedral coordination
(b) The presence of hydrogen bonds
(c) The presence of polar groups

27 The process by which polycrystalline solids can be made ferroelectric is:
(a) Annealing
(b) Sintering
(c) Poling

Calculations and questions

11.1 The plates on a parallel plate capacitor are separated by 0.1 mm and filled with air.
(a) What is the capacitance if the plates have an area of 1 cm^2?
(a) If the space between the plates is filled with a polyethylene sheet, with a relative permittivity of 2.3, what is the new capacitance?

11.2 A parallel plate capacitor is connected to a battery and acquires a charge of 200 μC on each plate. A polymer is inserted and the charge on the plates is now found to be 750 μC. What is the relative permittivity of the polymer?

11.3 A parallel plate capacitor has a capacitance of 8 nF and is to be operated under a voltage of 80 V. What is the relative permittivity of the dielectric if the maximum dimensions of the capacitor are 1 mm × 1 cm × 1 cm?

11.4 The dipole moment of the molecule nitric oxide, NO, is 0.5×10^{-30} C m. The N–O bond length is 0.115 nm.

(a) What is the charge on the atoms?

(b) Which atom is more positive?

11.5 The dipole moment of a water molecule is 6.2×10^{-30} C m, the H–O bond length is 95.8 pm and the H–O–H bond angle is 104.5°. Determine the charge on each atom.

11.6 The dipole moment of the molecule HCN is 9.8×10^{-30} C m and the charges, which reside on the H and N atoms (with carbon central), are measured to be 3.83×10^{-20} C.

(a) What is the dipole length and hence the approximate length of the molecule?

(b) The molecules are packed into a cubic structure, with a lattice parameter of 0.512 nm, each unit cell containing one molecule at $(0, 0, 0)$. Determine the bulk polarisation of the solid when all dipoles are aligned.

11.7 The dipole moments of the following molecules are:

- carbon monoxide, CO (linear), 0.334×10^{-30} C m;
- nitrous oxide, N_2O (linear), 0.567×10^{-30} C m;
- ammonia, NH_3 (tetrahedral, N at one vertex, H–N–H bond angle = 106.6°), 4.837×10^{-30} C m;
- sulphur dioxide, SO_2 (angular, O–S–O bond angle = 119.5°), 5.304×10^{-30} C m.

The covalent radii of the atoms involved are: C, 0.077 nm; O, 0.074 nm; N, 0.074 nm; H, 0.037 nm; S, 0.104 nm. Calculate the nominal charges on the atoms as a fraction of the electron charge.

11.8 Derive the Clausius–Mosotti equation using text Equations (11.3), (11.4) and (11.5). [Note: derivation is not given in the answers at the end of this book.]

11.9 The following data are for a single crystal of periclase, MgO: relative permittivity, ε_r, 9.65; refractive index, n, 1.736; cubic unit cell, a_0, 0.4207 nm, $Z = 4$ formula units of MgO.

(a) Estimate (i) the electronic polarisability and (ii) the corresponding polarisability volume.

(b) Estimate (i) the ionic polarisability and (ii) the corresponding polarisability volume.

11.10 The following data are for a single crystal of α-quartz, one of the mineral forms of SiO_2: average relative permittivity, ε_r, 4.477; average refractive index, n, 1.5485; hexagonal unit cell, a_0, 0.49136 nm, c_0, 0.54051 nm, $Z = 3$ formula units of SiO_2. Quartz is hexagonal, which means that the refractive indices and relative permittivity depend on crystallographic direction (see Table 14.1) and the Clausius–Mossotti and Lorentz–Lorentz relations apply only approximately. Nevertheless, from the data given:

(a) Estimate (i) the electronic polarisability and (ii) the corresponding polarisability volume.

(b) Estimate (i) the ionic polarisability and (ii) the corresponding polarisability volume.

11.11 Use the additivity rule to estimate (a) the ionic, (b) the electronic and (c) the total polarisability of forsterite, Mg_2SiO_4, given the information in Questions 11.9 and 11.10, assuming that only ionic and electronic polarisations are important.

11.12 Use the following crystallographic and optical data for forsterite to estimate the electronic polarisability of the mineral: forsterite is orthorhombic, $a_0 = 0.4758\,\text{nm}$, $b_0 = 1.0214\,\text{nm}$, $c_0 = 0.5984\,\text{nm}$, $Z = 4$ formula units of Mg_2SiO_4. The three principle refractive indices are 1.635, 1.651 and 1.670.

11.13 Estimate (a) the polarisability and (b) the relative permittivity of the garnet $Ca_3Ga_2Ge_3O_{12}$, using the following data: $Ca_3Ga_2Ge_3O_{12}$, cubic, $a_0 = 1.2252\,\text{nm}$, $Z = 8$; CaO, polarisability, α, $5.22 \times 10^{-30}\,\text{m}^3$; Ga_2O_3, polarisability, α, $8.80 \times 10^{-30}\,\text{m}^3$; GeO_2, polarisability, α, $5.50 \times 10^{-30}\,\text{m}^3$.

11.14 The relative permittivity of the garnet $Y_3Fe_5O_{12}$, a magnetic oxide, was measured as 15.7. Calculate (a) the polarisability and (b) the volume polarisability of Y_2O_3 if the volume polarisability given for Fe_2O_3 is $10.5 \times 10^{-30}\,\text{m}^3$. The unit cell of $Y_3Fe_5O_{12}$ is cubic, $a_0 = 1.2376\,\text{nm}$, $Z = 8$ formula units of $Y_3Fe_5O_{12}$.

11.15 Use the additivity rule to estimate (a) the polarisability and (b) the volume polarisability of mullite, Al_2SiO_5. The following volume polarisabilities were found in the literature: SiO_2, $4.84 \times 10^{-30}\,\text{m}^3$; Al_2O_3, $7.70 \times 10^{-30}\,\text{m}^3$. The experimental value is $15.22 \times 10^{-30}\,\text{m}^3$; (c) comment on the accuracy of the method.

11.16 Use the additivity rule to estimate (a) the polarisability and (b) the volume polarisability of diopside, $CaMgSi_2O_6$. The following volume polarisabilities were found in the literature. Magnesium oxide, MgO, $3.32 \times 10^{-30}\,\text{m}^3$, SiO_2, $4.84 \times 10^{-30}\,\text{m}^3$; CaO, $5.22 \times 10^{-30}\,\text{m}^3$. The experimental value of the volume polarisability is $18.78 \times 10^{-30}\,\text{m}^3$; (c) comment on the accuracy of the method.

11.17 The polarisability for the oxide $Mn_3Al_2Si_3O_{10}$ was estimated to be $35.83 \times 10^{-30}\,\text{C}\,\text{m}^2\,\text{V}^{-1}$. Determine the value of the polarisability for Mn^{2+} ions in this oxide given the following data: α (Al^{3+}), $0.32 \times 10^{-30}\,\text{C}\,\text{m}^2\,\text{V}^{-1}$; α (Si^{4+}), $0.11 \times 10^{-30}\,\text{C}\,\text{m}^2\,\text{V}^{-1}$; α (O^{2-}), $2.64 \times 10^{-30}\,\text{C}\,\text{m}^2\,\text{V}^{-1}$.

11.18 Show that the units for the direct piezoelectric coefficient, d, of $\text{C}\,\text{N}^{-1}$ and $\text{m}\,\text{V}^{-1}$ are equivalent. [Note: answer is not shown at the end of this book.]

11.19 The relevant value of the piezoelectric coefficient, d, for a quartz is given as $2.3\,\text{pC}\,\text{N}^{-1}$. Calculate the polarisation of a plate of dimensions $10\,\text{cm} \times 5\,\text{cm} \times 0.5\,\text{mm}$ when a mass of 0.5 kg is placed on it.

11.20 An electret film with the very high piezoelectric coefficient of $170\,\text{pC}\,\text{N}^{-1}$ is used in speakers, microphones and keyboards and related devices where mechanical and electrical signals are coupled. Calculate the change in thickness when 500 V are applied across a film 0.1 mm thick.

11.21 The semiprecious gemstone tourmaline, with an approximate formula $CaLi_2Al_7(OH)_4(BO_3)_3Si_6O_{18}$, has a pyroelectric coefficient, π_i, of $4 \times 10^{-6}\,\text{C}\,\text{m}^{-2}\,\text{K}^{-1}$. The unique polar axis is the crystallographic c axis. What is the change in polarisation caused by a change of temperature of 100 °C?

11.22 The measured relative permittivity, ε_r, of a ceramic sample of $PbZrO_3$ as a function of temperature, T, is given in Table 11.3. Determine (a) the Curie temperature, T_c, and (b) the Curie constant, C, for this sample.

Table 11.3 Data for question 11.22

ε_r	130	142	166	222	360	420	472	556
T/°C	50	100	150	200	225	230	234	235
ε_r	775	3200	3000	2840	2440	1620	1240	840
T/°C	236	238	240	242	250	275	300	350

11.23 The measured relative permittivity, ε_r, of a ceramic sample of $Cd_2Nb_2O_7$ as a function of temperature, T, is given in Table 11.4. Determine (a) the Curie temperature, T_c and (b) the Curie constant, C, for this sample.

Table 11.4 Data for question 11.23

ε_r	4500	4125	3750	3500	3225	3000	2800	2600
$T/°C$	−80	−75	−70	−65	−60	−55	−50	−45
ε_r	2465	2280	2115	2000	1860	1750	1630	1560
$T/°C$	−40	−35	−30	−25	−20	−15	−10	−5

11.24 The measured relative permittivity, ε_r, of a crystal of triglycine sulphate as a function of temperature, T, is given in Table 11.5. Determine (a) the Curie temperature, T_c, and (b) the Curie constant, C, for triglycine sulphate.

Table 11.5

ε_r	120	190	280	400	540	730	1300	~7000
$T/°C$	40	41	42	43	44	45	46	47
ε_r	1100	830	700	590	520	460	420	380
$T/°C$	48	49	50	51	52	53	54	55
ε_r	250	180	130	110				
$T/°C$	60	65	70	75				

11.25 Zincite (zinc oxide, ZnO) has a hexagonal unit cell, with $a_0 = 0.3250$ nm, $c_0 = 0.5207$ nm and a unit cell volume of 47.63×10^{-27} m^3. The atom positions are Zn, $(\frac{1}{3}, \frac{2}{3}, 0)$, $(\frac{2}{3}, \frac{1}{3}, \frac{1}{2})$; O, $(\frac{1}{3}, \frac{2}{3}, 0.38)$, $(\frac{2}{3}, \frac{1}{3}, 0.58)$. There are two formula units of ZnO in the unit cell. (a) Sketch the unit cell [sketch not shown at the end of this book] and (b) estimate the maximum spontaneous polarisation of ZnO, assuming that the structure is ionic.

11.26 Calculate the maximum spontaneous polarisation of a crystal of sodium nitrite, $NaNO_2$, given that the unit cell is orthorhombic, with $a_0 = 0.360$ nm, $b_0 = 0.575$ nm, $c_0 = 0.535$ nm, Z = two formula units of $NaNO_2$. The dipole moment of each N–O bond is 0.5×10^{-30} C m^{-1}, and the O–N–O angle is 115°.

11.27 (a) Calculate the dipole moment of a TiO_6 octahedron in $BaTiO_3$, with a very slightly distorted perovskite structure, in which $a_0 = 0.3997$ nm, $c_0 = 0.4031$ nm, tetragonal, assuming that the compound is fully ionic and that the Ti^{4+} ions are displaced by 0.012 nm along the c axis of the unit cell. (b) Determine the maximum spontaneous polarisation under these conditions.

11.28 (a) Calculate the dipole moment of an NbO_6 octahedron in $KNbO_3$, with a very slightly distorted perovskite structure, in which $a_0 = 0.4002$ nm, $c_0 = 0.4064$ nm, tetragonal, assuming that the compound is fully ionic and that the Nb^{5+} ions are displaced by 0.017 nm along the c axis of the unit cell. (b) Determine the maximum spontaneous polarisation under these conditions.

11.29 (a) Calculate the dipole moment of a TiO_6 octahedron in $PbTiO_3$, with a very slightly distorted perovskite structure, in which $a_0 = 0.3899$ nm, $c_0 = 0.4153$ nm, tetragonal, assuming that the compound is fully ionic and that the Ti^{4+} ions are displaced by 0.030 nm along the c axis of the unit cell. (b) Determine the maximum spontaneous polarisation under these conditions.

11.30 Most ceramics are electrical insulators. Describe the combination of factors that would allow a ceramic to be classified as a ferroelectric rather than just an insulator. [Note: answer is not provided at the end of this book.]

11.31 Both silica glass and quartz, SiO_2, are composed of SiO_4 tetrahedra and neither material posses a centre of symmetry. Why is silica glass not a piezoelectric, whereas quartz is? [Note: answer is not provided at the end of this book.]