

Section 14: Dielectric properties of insulators

The central quantity in the physics of dielectrics is the polarization of the material \mathbf{P} . The polarization \mathbf{P} is defined as the dipole moment \mathbf{p} per unit volume. The dipole moment of a system of charges is given by

$$\mathbf{p} = \sum_i q_i \mathbf{r}_i \quad (1)$$

where \mathbf{r}_i is the position vector of charge q_i . The value of the sum is independent of the choice of the origin of system, provided that the system is neutral. The simplest case of an electric dipole is a system consisting of a positive and negative charge, so that the dipole moment is equal to qa , where \mathbf{a} is a vector connecting the two charges (from negative to positive). The electric field produced by the dipole moment at distances much larger than a is given by (in CGS units)

$$\mathbf{E}(\mathbf{r}) = \frac{3(\mathbf{p} \cdot \mathbf{r})\mathbf{r} - r^2\mathbf{p}}{r^5} \quad (2)$$

According to electrostatics the electric field \mathbf{E} is related to a scalar potential as follows

$$\mathbf{E} = -\nabla \varphi, \quad (3)$$

which gives the potential

$$\varphi(\mathbf{r}) = \frac{\mathbf{p} \cdot \mathbf{r}}{r^3} \quad (4)$$

When solving electrostatics problem in many cases it is more convenient to work with the potential rather than the field.

A dielectric acquires a polarization due to an applied electric field. This polarization is the consequence of redistribution of charges inside the dielectric. From the macroscopic point of view the dielectric can be considered as a material with no net charges in the interior of the material and induced negative and positive charges on the left and right surfaces of the dielectric. The fact that the average charge inside the dielectric is zero can be understood if we take a macroscopic volume, it will contain equal amount of positive and negative charges and the net charge will be zero. On the other hand if we consider a volume including a boundary perpendicular to the direction of polarization, there is a net positive (negative) charge on the surface which is not compensated by charges inside the dielectric. Therefore, the polarization charge appears on the surface on the dielectric.

Polarization of the dielectric produces a macroscopic electric field, which is determined by these surface charges. This can be seen from the following consideration. The electrostatic potential (4) produced by a dipole can be represented as

$$\varphi(\mathbf{r}) = \mathbf{p} \cdot \nabla \frac{1}{r}. \quad (5)$$

Therefore for a volume distribution of the polarization we have:

$$\varphi(\mathbf{r}) = \int dV \left(\mathbf{P}(r') \cdot \nabla \frac{1}{|\mathbf{r} - \mathbf{r}'|} \right), \quad (6)$$

where the integration is performed over the volume of the dielectric. Assuming for simplicity that the polarization \mathbf{P} is constant throughout the medium and applying the Gauss theorem we obtain:

$$\varphi(\mathbf{r}) = \int dV \left(\nabla \frac{\mathbf{P}}{|\mathbf{r} - \mathbf{r}'|} \right) = \int dS \frac{\mathbf{n} \cdot \mathbf{P}}{|\mathbf{r} - \mathbf{r}'|} = \int dS \frac{\sigma}{|\mathbf{r} - \mathbf{r}'|}. \quad (7)$$

where the integration is performed over the surface of the dielectric and $\sigma = \mathbf{n} \cdot \mathbf{P}$ is the fictitious surface charge density. Here \mathbf{n} is the unit normal to the surface, directed outward from the polarized medium.

Using the potential (7) we can easily calculate the electric field due to the uniform polarization \mathbf{P} . Note that this field is macroscopic. It is a smooth function on atomic scale because we replaced the discrete lattice dipoles with the smoothed polarization \mathbf{P} .

The total macroscopic electric field \mathbf{E} is the sum the applied field \mathbf{E}_0 and the field \mathbf{E}_1 is the field due to the polarization of the solid:

$$\mathbf{E} = \mathbf{E}_0 + \mathbf{E}_1. \quad (8)$$

The field \mathbf{E}_1 is called the *depolarization field*, for within the body it tends to oppose the applied field \mathbf{E}_0 as in Fig. 1.

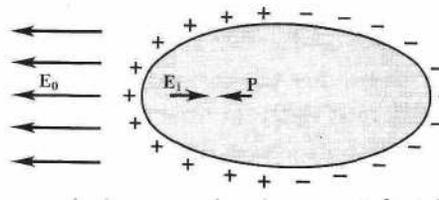


Fig.1 The depolarization field \mathbf{E}_1 is opposite to \mathbf{P} . The fictitious surface charges are indicated: the field of these charges is \mathbf{E}_1 within the ellipsoid.

It can be shown that for specimens in the shape of ellipsoids, a class that includes spheres, cylinders, and discs as limiting forms, have an advantageous property: a uniform polarization produces a uniform depolarization field inside the body. If P_x, P_y, P_z are the components of the polarization \mathbf{P} referred to the principal axes of an ellipsoid, then the components of the depolarization field are written as

$$E_{1x} = -N_x P_x; \quad E_{1y} = -N_y P_y; \quad E_{1z} = -N_z P_z. \quad (9)$$

Here N_x, N_y, N_z are the *depolarization factors*; their values depend on the ratios of the principal axes of the ellipsoid. The N 's are positive and satisfy the sum rule $N_x + N_y + N_z = 4\pi$ in CGS. For example, for a sphere $N_x = N_y = N_z = 4\pi/3$. For a thin slab, normal to the slab $N_z = 4\pi$ and $N_x = N_y = 0$.

The polarization is induced by electric field and therefore it is a function of electric field. The relationship is written in the following way

$$\mathbf{P} = \chi \mathbf{E}. \quad (10)$$

where χ is the *dielectric susceptibility*. In general χ is a tensor and depends on electric field. Note that the electric field which enters this formula is the macroscopic field (8), which includes both the external field and the depolarization field.

If the dielectric is an ellipsoid and a uniform applied field \mathbf{E}_0 is applied parallel to the principal axis of the ellipsoid, then

$$E = E_0 + E_1 = E_0 - NP. \quad (11)$$

and therefore

$$P = \chi E = \chi(E_0 - NP), \quad (12)$$

which gives

$$P = \frac{\chi}{1 + N\chi} E_0. \quad (13)$$

As is seen the value of the polarization depends on the depolarization factor N .

Local electric field at an atom

The value of the local electric field that acts at the site of an atom is significantly different from the value of the macroscopic electric field. The reason of that is that by definition the macroscopic field is the field which is averaged over large number of dipoles. On the other hand the local field which acts on a particular atom is influenced by the nearest surrounding and therefore can deviate from the average field.

As an example we consider the local field at a site with a cubic arrangement of neighbors in a crystal of spherical shape. The macroscopic electric field in a sphere is

$$\mathbf{E} = \mathbf{E}_0 + \mathbf{E}_1 = \mathbf{E}_0 - \frac{4\pi}{3} \mathbf{P}. \quad (14)$$

Now we consider the field that acts on the atom at the center of the sphere. If all dipoles are parallel to the z axis and have magnitude p , the z component of the field at the center due to all other dipoles is, according to (2), given by

$$\mathbf{E}_{loc} = \mathbf{E}_0 + \mathbf{E}_{dip} = \mathbf{E}_0 + \sum_i \frac{3(\mathbf{p} \cdot \mathbf{r}_i)\mathbf{r}_i - r_i^2 \mathbf{p}}{r_i^5} = \mathbf{E}_0 + \mathbf{p} \sum_i \frac{3z_i^2 - r_i^2}{r_i^5} = \mathbf{E}_0 \quad (15)$$

The latter equation comes from the fact that the x , y , z directions are equivalent because of the symmetry of the lattice and of the sphere; thus

$$\sum_i \frac{x_i^2}{r_i^5} = \sum_i \frac{y_i^2}{r_i^5} = \sum_i \frac{z_i^2}{r_i^5} \quad (16)$$

The correct local field is just equal to the applied field, $\mathbf{E}_{loc} = \mathbf{E}_0$, for an atom site with a cubic environment in a spherical specimen. Thus the local field is not the same as the macroscopic average field \mathbf{E} .

We now develop an expression for the local field at a general lattice site, not necessarily of cubic symmetry.

To evaluate \mathbf{E}_{loc} we must calculate the total field acting on a certain typical dipole, this field being due to the external field as well as all *other* dipoles in the system. This was done by Lorentz as follows: The dipole is imagined to be surrounded by a spherical cavity whose radius R is sufficiently large that the matrix lying outside it may be treated as a *continuous medium* as far as the dipole is concerned (Fig.2a). The interaction of our dipole with the other dipoles lying inside the cavity is, however, to be treated microscopically, which is necessary since the discrete nature of the medium very close to the dipoles should be taken into account. The local field, acting on the central dipole, is thus given by the sum

$$\mathbf{E}_{loc} = \mathbf{E}_0 + \mathbf{E}_1 + \mathbf{E}_2 + \mathbf{E}_3. \quad (17)$$

where

\mathbf{E}_0 is the external field,

\mathbf{E}_1 is the depolarization field, i.e. the field due to the polarization charges lying at the external surfaces of the sample,

\mathbf{E}_2 the field due to the polarization charges lying on the surface of the Lorentz sphere, which is known as Lorentz field.

and \mathbf{E}_3 is the field due to other dipoles lying within the sphere.

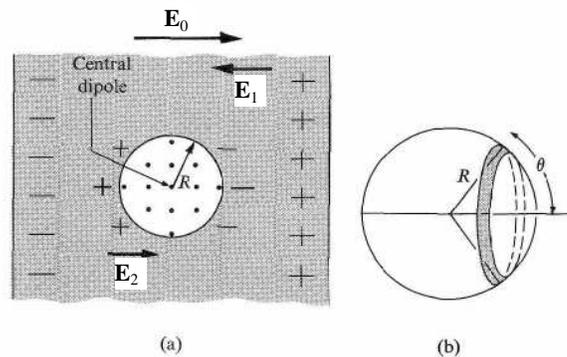


Fig.2 (a) The procedure for computing the local field, (b) The procedure for calculating E_2 , the field due to the polarization charge on the surface of the Lorentz sphere.

Note that the part of the medium between the sphere and the external surface does not contribute anything since, the volume polarization charges compensate each other, resulting in a zero net charge in this region.

The contribution $\mathbf{E}_1 + \mathbf{E}_2 + \mathbf{E}_3$ to the local field is nothing but the total field at one atom caused by the dipole moments of all the other atoms in the specimen. Dipoles at distances greater than perhaps ten lattice constants from the reference site make a smoothly varying contribution, a contribution which may be replaced by two surface integrals. One surface integral is taken over the outer surface of the ellipsoidal specimen and defines \mathbf{E}_1 , as in Eq.(7). The second surface integral defines \mathbf{E}_2 and may be taken over any interior surface that is a suitable distance from the reference

site. We count in \mathbf{E}_3 any dipoles not included in the volume bounded by the inner and outer surfaces. It is convenient to let the interior surface be spherical.

Lorentz field, \mathbf{E}_2 :

The polarization charges on the surface of the Lorentz cavity may be considered as forming a continuous distribution. The density of the surface charge is equal to $\mathbf{P}\cos\theta$. The field due to the charge at a point located at the center of the sphere is, according to Coulomb's law, given by

$$\mathbf{E}_2 = \int_0^\pi \left(\frac{\mathbf{P}\cos\theta}{R^2} \right) \cos\theta (2R^2 \sin\theta d\theta) = \frac{4\pi}{3} \mathbf{P}. \quad (18)$$

where the additional factor $\cos\theta$ is included because we are evaluating only the component of the field along the direction of \mathbf{P} (other components vanish by symmetry), and the factor $2R^2 \sin\theta d\theta$ is the surface element along the sphere (see Fig. 2b). Integration of (18) leads to the simple result a field in the same direction as the external field.

Field of dipoles inside cavity, \mathbf{E}_3 :

The field \mathbf{E}_3 due to the dipoles within the spherical cavity is the only term that depends on the crystal structure. We showed for a reference site with cubic surroundings in a sphere that $\mathbf{E}_3 = 0$ if all the atoms may be replaced by point dipoles parallel to each other.

The total local field at a cubic site is, then,

$$\mathbf{E}_{loc} = \mathbf{E}_0 + \mathbf{E}_1 + \frac{4\pi}{3} \mathbf{P} = \mathbf{E} + \frac{4\pi}{3} \mathbf{P}. \quad (19)$$

This is known as *the Lorentz relation*: the field acting at an atom in a cubic site is the macroscopic field \mathbf{E} of plus $4\pi\mathbf{P}/3$ from the polarization of the other atoms in the specimen. Experimental data for cubic ionic crystals support the Lorentz relation.

The difference between \mathbf{E} , which is known as the *Maxwell field* and the local field \mathbf{E}_{loc} may be explained as follows. The field \mathbf{E} is a macroscopic quantity, and as such is an average field, the average being taken over a large number of molecules (Fig. 3). It is this field which enters into the Maxwell equations, which are used for the macroscopic description of dielectric media. In the present situation the field \mathbf{E} is a constant throughout the medium.

On the other hand, the local field \mathbf{E}_{loc} is a *microscopic* field which fluctuates rapidly within the medium. As the figure indicates, this field is quite large at the molecular sites themselves.

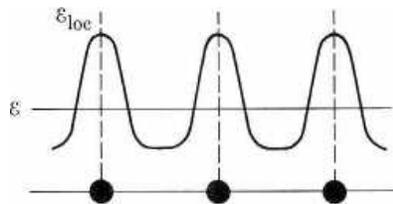


Fig. 3 The difference between the Maxwell field \mathbf{E} and the local field \mathbf{E}_{loc} . Solid circles represent molecules.

Dielectric constant and polarizability

The *dielectric constant* ϵ of an isotropic or cubic medium relative to vacuum is defined in terms of the macroscopic field E :

$$\epsilon = \frac{E + 4\pi P}{E} = 1 + 4\pi\chi. \quad (20)$$

Since the polarization of the medium is produced by the field it is convenient to define *the polarizability* α of an atom in terms of the local electric field at the atom:

$$\mathbf{p} = \alpha \mathbf{E}_{loc}. \quad (21)$$

where \mathbf{p} is the dipole moment. For a non-spherical atom α will be a tensor.

The polarization of a crystal may be expressed approximately as the product of the polarizabilities of the atoms times the local electric field:

$$\mathbf{P} = \sum_i N_i \mathbf{p}_i = \sum_i N_i \alpha_i \mathbf{E}_{loc}(i) \quad (22)$$

where N_i is the concentration and α_i the polarizability of atoms i , and $\mathbf{E}_{loc}(i)$ is the local field at atom sites i .

We want to relate the dielectric constant to the polarizabilities; the result will depend on the relation that holds between the macroscopic electric field and the local electric field.

If the local field is given by the Lorentz relation (19), then

$$\mathbf{P} = \left(\sum_i N_i \alpha_i \right) \left(\mathbf{E} + \frac{4\pi}{3} \mathbf{P} \right) \quad (23)$$

and we solve for \mathbf{P} to find the susceptibility

$$\chi = \frac{P}{E} = \frac{\sum_i N_i \alpha_i}{1 - \frac{4\pi}{3} \sum_i N_i \alpha_i} \quad (24)$$

Using Eq.(20) we can then write the expression in terms of the dielectric constant:

$$\frac{\epsilon - 1}{\epsilon + 2} = \frac{4\pi}{3} \sum_i N_i \alpha_i. \quad (25)$$

This is *the Clausius-Mossotti relation*. This relates the dielectric constant to the electronic polarizability, but only for crystal structures for which the Lorentz local field (19) holds.

Sources of polarizability

Now we examine more closely the physical process which gives rise to polarizability. Basically, polarizability is a consequence of the fact that the molecules, which are the building blocks of all substances, are composed of both positive charges (nuclei) and negative charges (electrons). When a field acts on a molecule, the positive charges are displaced along the field, while the negative charges are displaced in a direction opposite to that of the field. The effect is therefore to pull the

opposite charges apart, i.e., to polarize the molecule. There are different types of polarization processes, depending on the structure of the molecules which constitute the solid. If the molecule has a *permanent moment*, i.e., a moment even in the absence of an electric field, we speak of a *dipolar* molecule, and a *dipolar* substance.

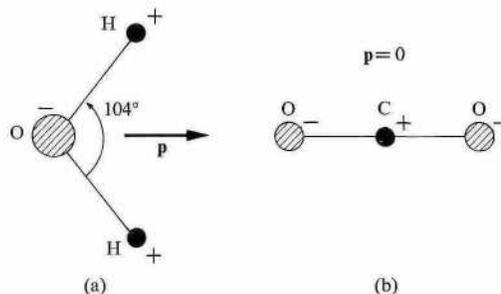


Fig.4 (a) The water molecule (b) CO₂ molecule.

An example of a dipolar molecule is the H₂O molecule in Fig.4a. The dipole moments of the two OH bonds add vectorially to give a nonvanishing net dipole moment. Some molecules are nondipolar, possessing no permanent moments; a common example is the CO₂ molecule in Fig.4b. The moments of the two CO bands cancel each other because of the rectilinear shape of the molecule, resulting in a zero net dipole moment.

The water molecule has a permanent moment because the two OH bands do not lie along the same straight line, as they do in the CO₂ molecule. The moment thus depends on the geometrical arrangement of the charges, and by measuring the moment one can therefore gain information concerning the structure of the molecule.

Despite the fact that the individual molecules in a dipolar substance have permanent moments, the net polarization vanishes in the absence of an external field because the molecular moments are randomly oriented, resulting in a complete cancellation of the polarization. When a field is applied to the substance, however, the molecular dipoles tend to align with the field, and this results in a net nonvanishing polarization. This leads to the so-called *dipolar polarizability*.

If the molecule contains ionic bonds, then the field tends to stretch the lengths of these bonds. This occurs in NaCl, for instance, because the field tends to displace the positive ion Na⁺ to the right (see Fig.5), and the negative ion Cl⁻ to the left, resulting in a stretching in the length of the bond. The effect of this change in length is to produce a net dipole moment in the unit cell where previously there was none. Since the polarization here is due to the relative displacements of oppositely charged ions, we speak of *ionic polarizability*.

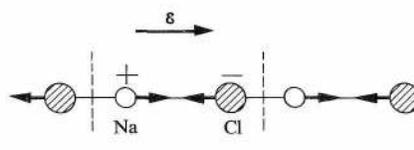


Fig.5 Ionic polarization in NaCl. The field displaces Na⁺ and Cl⁻ ions in opposite directions, changing the bond length.

Ionic polarizability exists whenever the substance is either ionic, as in NaCl, or dipolar, as in H₂O, because in each of these classes there are ionic bonds present. But in substances in which such bonds are missing - such as Si and Ge - ionic polarizability is absent.

The third type of polarizability arises because the individual ions or atoms in a molecule are themselves polarized by the field. In the case of NaCl, each of the Na⁺ and Cl⁻ ions are polarized. Thus the Na⁺ ion is polarized because the electrons in its various shells are displaced to the left relative to the nucleus, as shown in Fig.6. We are clearly speaking here of *electronic polarizability*.

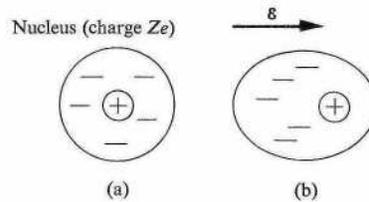


Fig. 6 Electronic polarization: (a) Unpolarized atom, (b) Atom polarized as a result of the field.

Electronic polarizability arises even in the case of a neutral atom, again because of the relative displacement of the orbital electrons.

In general, therefore, the total polarizability is given by

$$\alpha = \alpha_e + \alpha_i + \alpha_d, \quad (26)$$

which is the sum of the electronic, ionic, and dipolar polarizabilities, respectively. The electronic contribution is present in any type of substance, but the presence of the other two terms depends on the material under consideration.

The relative magnitudes of the various contributions in (26) are such that in nondipolar, ionic substances the electronic part is often of the same order as the ionic. In dipolar substances, however, the greatest contribution comes from the dipolar part. This is the case for water, as we shall see.

Another important distinction between the various polarizabilities emerges when one examines the behavior of the ac polarizability that is induced by an alternating field. Figure 7 shows a typical dependence of this polarizability on frequency over a wide range, extending from the static all the way up to the ultraviolet region. It can be seen that in the range from $\omega = 0$ to $\omega = \omega_d$, where ω_d (d for dipolar) is some frequency usually in the microwave region, the polarizability is essentially constant. In the neighborhood of ω_d , however, the polarizability decreases by a substantial amount. This amount corresponds precisely, in fact, to the dipolar contribution α_d . The reason for the disappearance of α_d in the frequency range $\omega > \omega_d$ is that the field now oscillates too rapidly for the dipole to follow, and so the dipoles remain essentially stationary.

The polarizability remains similarly unchanged in the frequency range from ω_d to ω_i and then drops down at the higher frequency. The frequency ω_i lies in the infrared region, and corresponds to the frequency of the transverse optical phonon in the crystal. For the frequency range $\omega > \omega_i$ the ions with their heavy masses are no longer able to follow the very rapidly oscillating field, and consequently the ionic polarizability α_i , vanishes, as shown in Fig. 7.

Thus in the frequency range above the infrared, only the electronic polarizability remains effective, because the electrons, being very light, are still able to follow the field even at the high frequency. This range includes both the visible and ultraviolet regions. At still higher frequencies (above the electronic frequency ω_e , however, the electronic contribution vanishes because even the electrons are too heavy to follow the field with its very rapid oscillations.

The frequencies ω_d and ω_i , characterizing the dipolar and ionic polarizabilities, respectively, depend on the substance considered, and vary from one substance to another. However, their orders of magnitude remain in the regions indicated above, i.e., in the microwave and infrared, respectively. The various polarizabilities may thus be determined by measuring the substance at various appropriate frequencies.

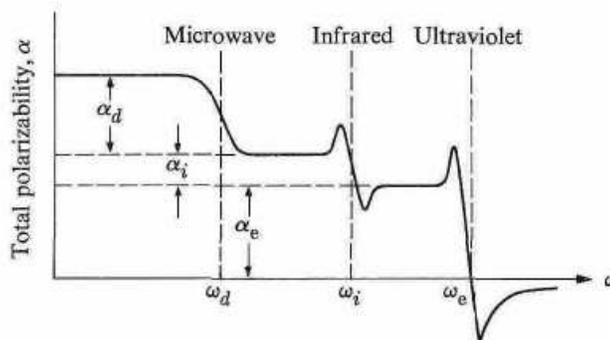


Fig.7 Frequency dependence of the several contributions to the polarizability.

Piezoelectricity

The term *piezoelectricity* refers to the fact that, when a crystal is strained, an electric field is produced within the substance. As a result of this field, a potential difference develops across the sample, and by measuring this potential one may determine the field. The inverse effect - that an applied field produces strain - has also been observed.

The piezoelectric effect is very small. A field of 10^3 V/cm in quartz (SiO_2) produces a strain of only 10^{-7} . That is, a rod 1 cm long changes its length by 10\AA . Conversely, even small strains can produce enormous electric fields.

The piezoelectric effect is often used to convert electrical energy into mechanical energy, and vice versa; i.e., the substance is used as a *transducer*. For instance, an electric signal applied to the end of a quartz rod generates a mechanical strain, which consequently leads to the propagation of a mechanical wave - a sound wave - down the rod. Quartz is the most familiar piezoelectric substance, and the one most frequently used in transducers.

The microscopic origin of piezoelectricity lies in the displacement of ionic charges within the crystal. In the absence of strain, the distribution of the charges at their lattice sites is symmetric, so the internal electric field is zero. But when the crystal is strained, the charges are displaced. If the charge distribution is no longer symmetric, then a net polarization, and a concomitant electric field, develops. It is this field which operates in the piezoelectric effect.

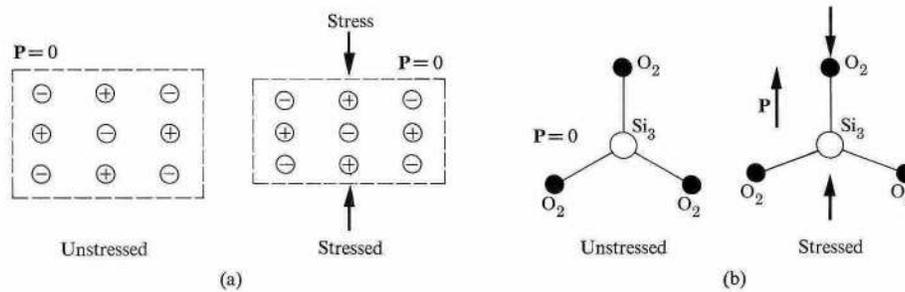


Fig. 8 Crystal with center of inversion exhibits no piezoelectric effect, (b) Origin of piezoelectric effect in quartz: crystal lacks a center of inversion.

It follows that a substance can be piezoelectric only if the unit cell *lacks a center of inversion*. Figure 8 (a) shows this, and demonstrates that if a center of inversion *is* present, it persists even after distortion, and consequently the polarization remains zero. However, when there is no center of inversion, as in Fig. 8 (b), distortion produces a polarization. We see, therefore, that no regular cubic lattice can exhibit piezoelectricity.

The lack of inversion center, however, is not sufficient to guarantee piezoelectricity, and only relatively few substances, exhibit this phenomenon.

Ferroelectricity

Ferroelectric crystal exhibits an electric dipole moment even in the absence of an external electric field. In the ferroelectric state the center of positive charge of the crystal does not coincide with the center of negative charge. The plot of polarizations versus electric field for the ferroelectric state shows a hysteresis loop. A crystal in a normal dielectric state usually does not show significant hysteresis when the electric field is increased and then reversed, both slowly.

In *ferroelectric* materials the ionic susceptibility is sensitive to variations in temperature. In these substances, the static dielectric constant changes with temperature according to the relation

$$\varepsilon = \frac{C}{T - T_c}, \quad (27)$$

where C is a constant independent of temperature.

This behavior is valid only in the temperature range $T > T_c$. In the range $T < T_c$, the material becomes *spontaneously* polarized, i.e., an electric polarization develops in it without the help of an external field. (This phenomenon is analogous to the spontaneous magnetization which takes place in ferromagnetic materials.)

A *phase transition* occurs at the temperature T_c . Above the transition temperature, the substance is in the *paraelectric phase*, in which the elementary dipoles of the various unit cells in the crystal are oriented randomly. The dielectric constant is shown in Fig.9a. Below the transition temperature, the elementary dipoles interact with each other, and this gives rise to an internal field, which lines up the dipoles. The direction of this field and the associated polarization lie in a certain favorable orientation in the crystal. Figure 9b shows the variation of the spontaneous polarization P with temperature for $T < T_c$. This polarization increases gradually as the temperature is lowered.

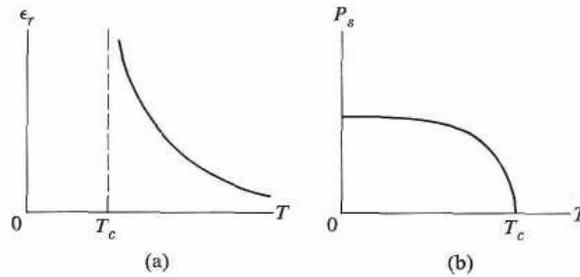


Fig. 9 (a) Dielectric constant ϵ versus T in a ferroelectric substance, (b) Spontaneous polarization P_s versus T in a ferroelectric substance.

Table 1 lists some crystals commonly considered to be ferroelectric, along with the transition temperature or Curie point T_C at which the crystal changes from the low temperature polarized state to the high temperature unpolarized state. Thermal motion tends to destroy the ferroelectric order. Some ferroelectric crystals have no Curie point because they melt before leaving the ferroelectric phase. The table also includes values of the spontaneous polarization P_S .

Table 1 Ferroelectric crystals

		T_C , in K	P_S , in $\mu\text{C cm}^{-2}$
KDP type	KH_2PO_4	123	4.75
	KD_2PO_4	213	4.83
	RbH_2PO_4	147	5.6
	KH_2AsO_4	97	5.0
	GeTe	670	—
TGS type	Tri-glycine sulfate	322	2.8
	Tri-glycine selenate	295	3.2
Perovskites	BaTiO_3	408	26.0
	KNbO_3	708	30.0
	PbTiO_3	765	>50
	LiTaO_3	938	50
	LiNbO_3	1480	71

Ferroelectric crystals may be classified into two main groups: *order-disorder* or *displacive*.

In ferroelectric materials exhibiting an order-disorder transition the displacements of atoms are about some double-well or multi-well configuration of sites in the paraelectric phase. In the ferroelectric phase the displacements are about an ordered subset of these wells. The order-disorder class of ferroelectrics includes crystals with hydrogen bonds in which the motion of the protons is related to the ferroelectric properties, as in potassium dihydrogen phosphate (KH_2PO_4) and isomorphous salts.

In ferroelectric materials exhibiting a displacive transition the atomic displacements represent oscillations about a nonpolar site in the paraelectric phase. After a displacive transition (ferroelectric phase) the oscillations are about a polar site. The displacive class of ferroelectrics includes ionic crystal structures closely related to the perovskite and ilmenite structures. The simplest ferroelectric crystal is GeTe with the sodium chloride structure.

As a concrete example of ferroelectric structure transformation, Fig. 10 shows the appropriate structure for BaTiO₃. Above the Curie temperature the structure is cubic, but as the temperature is lowered to T_C , the Ba²⁺ and Ti⁴⁺ ions are displaced as shown, producing a slightly compressed cubic structure. Although the displacement is small - only about 0.15Å - it is enough to give the observed polarization.

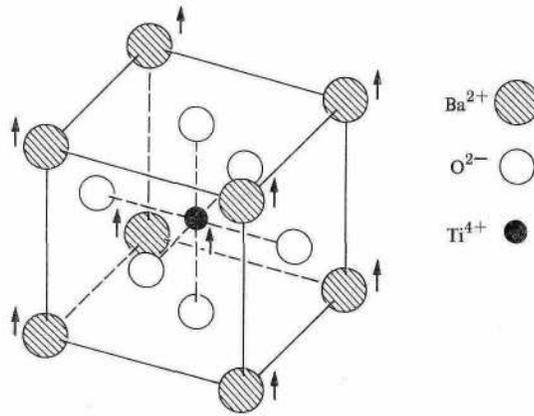


Fig. 10 Structure of BaTiO₃ in cubic phase (above T_C).

The occurrence of ferroelectricity in many perovskite-structure crystals suggests that this structure is favorably disposed to a displacive transition. Local field calculations make clear the reason for the favored position of this structure: the O²⁻ ions do not have cubic surroundings, and the local field factors turn out to be unusually large.

We give a simple form of the microscopic theory of ferroelectric transition, supposing that the local field at all atoms is equal to $\mathbf{E}_{loc} = \mathbf{E}_0 + \mathbf{E}_1 + \frac{4\pi}{3}\mathbf{P} = \mathbf{E} + \frac{4\pi}{3}\mathbf{P}$. We rewrite the Clausius-Mossotti relation (25) for the dielectric constant in the form

$$\epsilon = \frac{1 + \frac{8\pi}{3} \sum_i N_i \alpha_i}{1 - \frac{4\pi}{3} \sum_i N_i \alpha_i}. \quad (28)$$

where α_i is the electronic plus ionic polarizability of an ion of type i and N_i is the number of ions i per unit volume. The dielectric constant becomes infinite and permits a finite polarization in zero applied field when

$$\sum_i N_i \alpha_i = \frac{3}{4\pi}. \quad (29)$$

This is the condition for a *polarization catastrophe*.

The value of ϵ in (29) is sensitive to small departures of $\sum_i N_i \alpha_i$ from the critical value $3/4\pi$. If we write

$$\frac{4\pi}{3} \sum_i N_i \alpha_i = 1 - 3s. \quad (30)$$

where $s \ll 1$, the dielectric constant in (28) becomes

$$\varepsilon \approx 1/s. \quad (31)$$

Suppose near the critical temperature s varies linearly with temperature:

$$s \approx (T - T_c)/C, \quad (32)$$

where C is a constant. Such a variation of s or $\sum_i N_i \alpha_i$ might come from normal thermal expansion of the lattice. The dielectric constant has therefore the form

$$\varepsilon = \frac{C}{T - T_c}, \quad (33)$$

close to the observed temperature variation in the paraelectric state, Fig. 11.

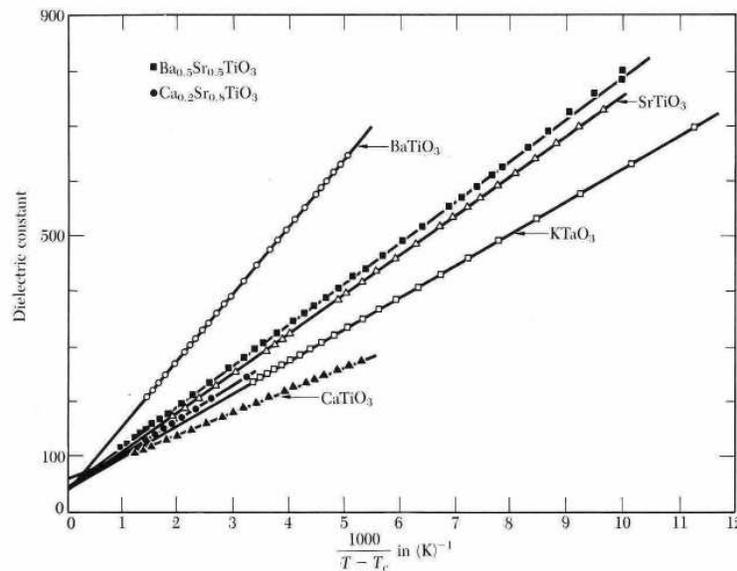


Fig.11 Dielectric constant versus $1/(T - T_c)$ in the paraelectric state ($T > T_c$) of perovskites.

The transition to ferroelectric state can be both the first- and second-order transitions. In a second-order transition there is no latent heat; the order parameter (in this instance, the polarization) is not discontinuous at the transition temperature. In a first-order transition the order parameter changes discontinuously at the transition temperature. For example, second order transition occurs in LiTaO_3 (Fig. 12) whereas the first order transition occurs in BaTaO_3 (Fig. 13).

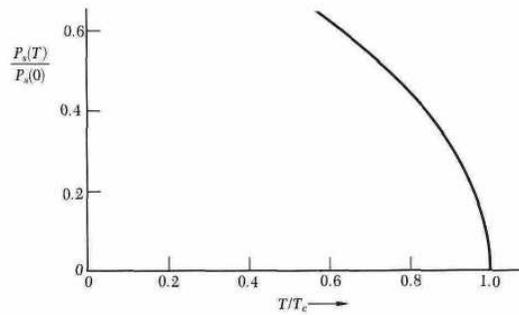


Fig.12 Spontaneous polarization in LiTaO3 versus temperature, for a second-order phase transition.

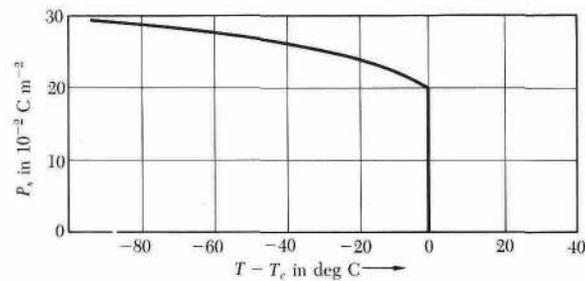


Fig. 13 Calculated values of the spontaneous polarization as a function of temperature for barium titanate.

Ferroelectric domains

A substance which is in its ferroelectric phase undergoes spontaneous polarization, but the *direction* of the polarization is not the same throughout the sample. The material is divided into a number of small *domains*, in each of which the polarization is constant. But the polarization in the different domains are different, so that the net total polarization of the whole sample vanishes in the equilibrium situation (Fig. 13).

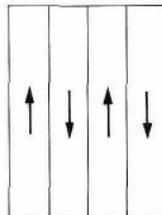


Fig. 13 Domain structure in an unpolarized ferroelectric sample.

When an external field is applied, the domains whose polarization is parallel to the field grow, while the domains of opposite polarization shrink. These growing and shrinking processes continue as the field increases until, at a sufficiently high field, the whole of the sample is polarized parallel to the field.