Functional Solid State Materials

- Electrical properties
- Optical properties
- Magnetic properties
- Mechanical properties

Materials & History

Stone age
Bronze age
Iron age
Silicon age

"the secret for transmuting base metals into precious gold"

Alchemist

Material Chemist

Development of Materials vs Human Society

The history of human society can be marked with inorganic materials.

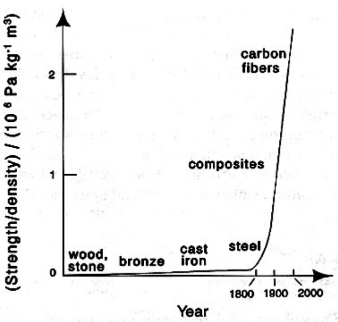
Historical Perspective

Stone → Bronze → Iron →Steel → Advanced materials

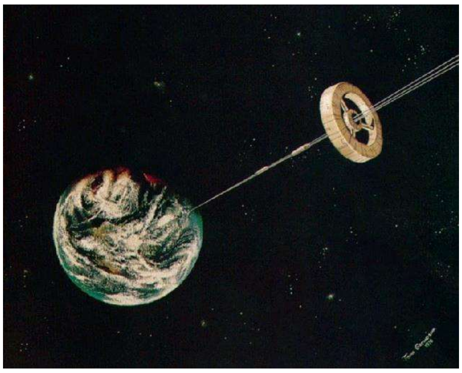
Historical Perspective

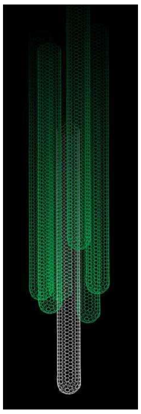
- Beginning of the Material Science — People began to make tools from stone — Start of the Stone Age about two million years ago.
- Natural materials: stone, wood, clay, skins, etc.
- The Stone Age ended about 5000 years ago with introduction of Bronze in the East Asia. Bronze is an alloy (copper + < 25% of tin + other elements).
- Bronze: can be hammered or cast into a variety of shapes, can be made harder by alloying, corrode only slowly after a surface oxide film forms.
- The Iron Age began about 3000 years ago and continues today. Use of iron and steel, a stronger and cheaper material changed drastically daily life of a common person.
- Age of Advanced Materials: throughout the Iron Age many new types of materials have been introduced (ceramic, semiconductors, polymers, composites…). Understanding of the relationship among structure, properties, processing, and performance of materials. Intelligent design of new materials.

Structure-Composition-Properties



A better understanding of structure-composition-properties relations has lead to a remarkable progress in properties of materials. Example is the dramatic progress in the strength to density ratio of materials, that resulted in a wide variety of new products, from dental materials to tennis racquets.



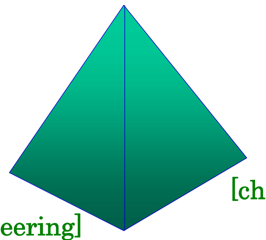


Types of Materials

Let us classify materials according to the way the atoms are bound together.

- Metals: valence electrons are detached from atoms, and spread in an “electron sea” that “glues” the ions together. Strong, ductile, conduct electricity and heat well, are shiny if polished.
- Semiconductors: the bonding is covalent (electrons are shared between atoms). Their electrical properties depend strongly on minute proportions of contaminants. Examples: Si, Ge, GaAs.
- Ceramics: atoms behave like either positive or negative ions, and are bound by Coulomb forces. They are usually combinations of metals or semiconductors with oxygen, nitrogen or carbon (oxides, nitrides, and carbides). Hard, brittle, insulators. Examples: glass, porcelain.
- Polymers: are bound by covalent forces and also by weak van der Waals forces, and usually based on C and H. They decompose at moderate temperatures (100–400°C), and are lightweight. Examples: plastic, rubber.

Materials Tetrahedron



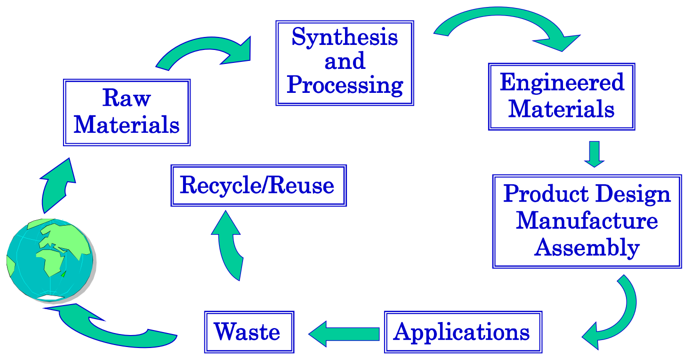
Performance [engineering]

Synthesis and Processing [chemistry & engineering]

Properties [chemistry & physics]

Structure and Composition [chemistry]

Life Cycle of Materials



Raw Materials

Synthesis and Processing

Engineered Materials

Product Design Manufacture Assembly

Applications

Waste

Recycle/Reuse

Properties

- Properties are the way the material responds to the environment and external forces.
- Mechanical properties — response to mechanical forces, strength, etc.
- Electrical and Magnetic properties — response to electrical and magnetic fields, conductivity, etc.
- Thermal properties are related to transmission of heat and heat capacity.
- Optical properties include to absorption, transmission and scattering of light.
- Chemical Stability in contact with the environment — corrosion resistance.

Electric Properties of Crystals

Crystals can be classified by electric properties:

- Conductors
- Dielectric crystals
- Semiconductors
- Superconductors

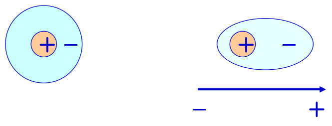
Dielectric Properties

The biggest difference between dielectric materials and conductors is that the transfer ways of electrons are totally different:

Dielectric —— in manner of induced polarization
conductor —— in manner of conduction

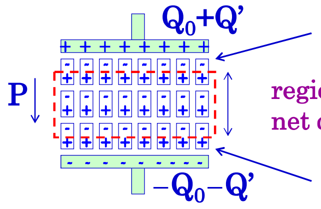
Dielectric Material

A dielectric material is an insulator in which electric dipoles can be induced by the electric field (or permanent dipoles can exist even without electric field), that is where positive and negative charge are separated on an atomic or molecular level.



Dielectric Materials

Dipole formation and/or orientation along the external electric field in the capacitor causes a charge redistribution so that the surface nearest to the positive capacitor plate is negatively charged and vice versa.



net negative charge at the surface, –Q'

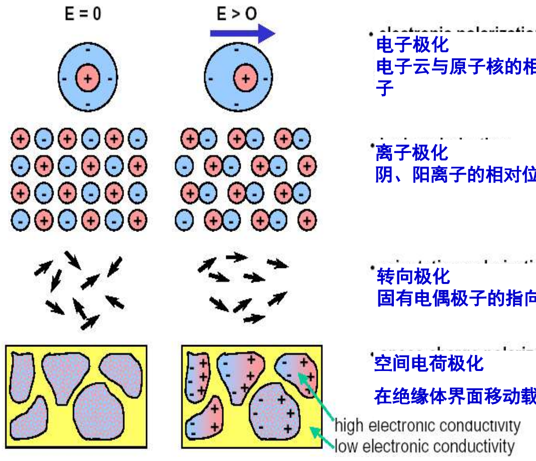
region of no net charge

net positive charge at the surface, Q' = PA

The process of dipole formation/alignment in electric field is called polarization and is described by P = Q'/A

极化类型

电介质的极化

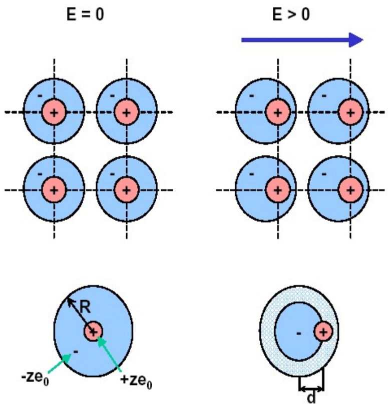


- 电子极化
  电子云与原子核的相对位移诱导电偶极子
- 离子极化
  阴、阳离子的相对位移诱导电偶极子
- 转向极化
  固有电偶极子的指向在外场中转向
- 空间电荷极化
  在绝缘体界面移动载流子形成的极化

high electronic conductivity

low electronic conductivity

电子极化



电子极化由电子云构成的负电荷中心($-Ze_0$)在外电场中相对于带正电的原子荷($+Ze_0$)的位移引起的

⇨ 电位移 |d|

- 诱导偶极子：

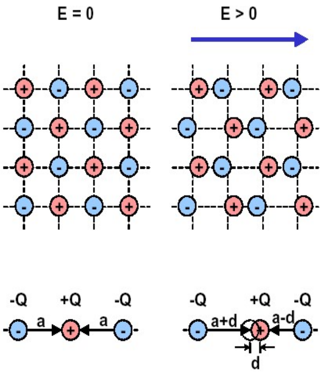
$$\boxed{p = z\cdot e_0\cdot d = \underbrace{4\pi\varepsilon_0\cdot R^3}_{微观极化率}\cdot E = \alpha_{el}\cdot E}$$

- 电极化率：

$$\boxed{\begin{aligned}\chi_{el} &= \frac{n\cdot\alpha_{el}}{\varepsilon_0} = 4\pi\cdot n\cdot R^3 \quad \text{i.e.}\\ \chi_{el} &= \sum_i 4\pi\cdot n_i\cdot R_i^{\,3}\end{aligned}}$$

n:原子/分子密度

离子极化



离子极化是由离子晶体中阳离子(＋Q)与阴离子(-Q)的位移引起的

⇨ 电位移 |d|

- 诱导偶极子：

$$\boxed{\begin{aligned}p &= \frac{Q}{2}\cdot(a+d-(a-d)) = Qd\\ k\cdot d &= Q\cdot E\\ p &= \frac{Q^2}{k}\cdot E = \alpha_{ion}\cdot E\end{aligned}}$$

微观极化率

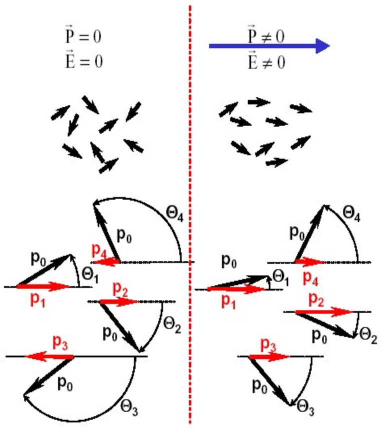
K_i描述了晶格的反作用力，K_i取决于晶格参数(离子间距，晶体结构，束缚能….）

- 电极化率：

$$\boxed{\chi_{ion} = \frac{n\cdot Q^2}{\varepsilon_0 k} \quad \text{i.e.} \quad \chi_{ion} = \sum_i \frac{n_i\cdot Q_i^{\,2}}{\varepsilon_0 k_i}}$$

Q: 离子电荷 N: 原子/分子密度

取向极化



- 电偶极矩pi

$$\boxed{p_i = p_0\cdot\cos\Theta_i}$$

分子电偶极矩pi

- 电极化强度P

$$\boxed{P = \frac{1}{V}\sum_{i=1}^{n} p_i}$$

- 平均微观极化率a_{or}

$$\boxed{\alpha_{or} \cong \frac{p_0^2}{3kT}}$$

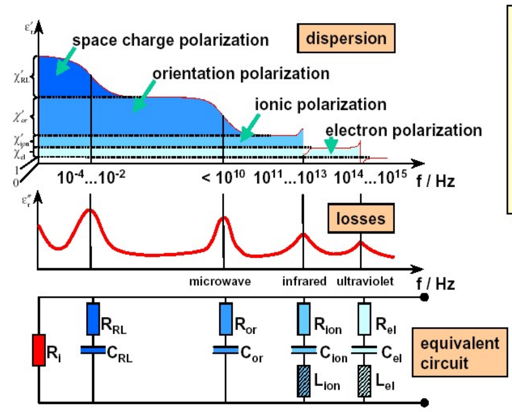
线性近似

- 电极化率c_{or}

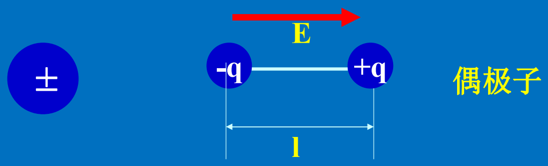
$$\boxed{\chi_{or} \cong \frac{n\cdot p_0^2}{3kT\cdot\varepsilon_0}}$$

Frequency Response (Switching Time)

介电
相对介电常数的频率依赖



drop out of polarization mechanism
- relaxation:
  space charge polarization
  orientation polarization
- resonance:
  ionic polarization
  electronic polarization



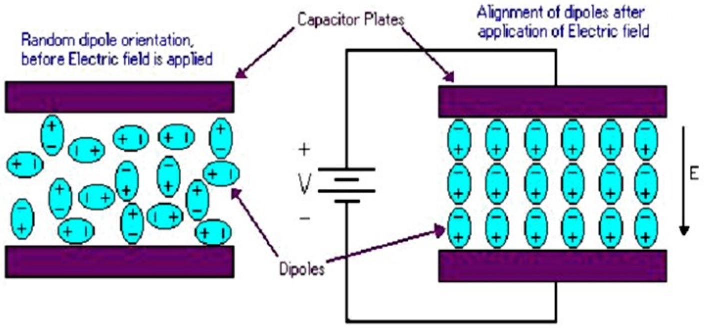
电偶极矩μ： μ=ql（单位：库仑 · 米）

电偶极矩的方向：负电荷指向正电荷。电偶极矩的方向与外电场的方向一致。

介质的极化强度P：P=∑ μ/V单位介质体积内的电偶极矩总和。或束缚电荷的面密度。

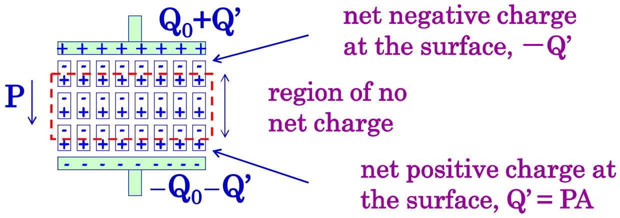
Dipole Moments

Orientation of dipole moments



Dielectric Materials

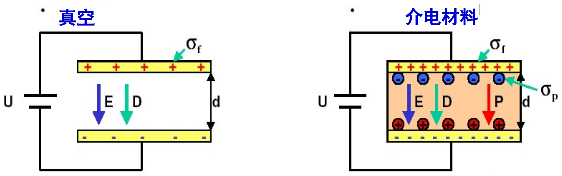
Dipole formation and/or orientation along the external electric field in the capacitor causes a charge redistribution so that the surface nearest to the positive capacitor plate is negatively charged and vice versa.



The process of dipole formation/alignment in electric field is called polarization and is described by P = Q'/A

宏观表征：从电路中定义

平行板电容器



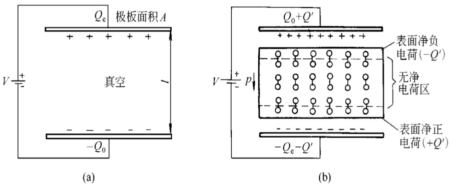
$$E=\frac{U}{d}=\frac{\sigma_f}{\varepsilon_0}$$
$$P=0$$
$$D=\sigma_f$$
$$D=\varepsilon_0\cdot E$$
$$C=\varepsilon_0\cdot\frac{A}{d}$$

E: 电场
D: 电位移
P: 极化强度
σ_f: 金属板表面的(正的与负的)自由电荷
σ_p: 介电材料表面的束缚电荷 (⊕ and ⊖)
ε_0: 真空介电常数(8.85×10^{-12}As/Vm)
ε_r: 相对介电常数
C: 电容

$$E=\frac{U}{d}=\frac{\sigma_f}{\varepsilon_0}=\frac{\sigma_p}{\varepsilon_r\cdot\varepsilon_0}$$
$$P=-\sigma_p$$
$$D=\sigma_f$$
$$D=\varepsilon_0\cdot E+P$$
$$C=\varepsilon_0\cdot\varepsilon_r\cdot\frac{A}{d}$$

电学性质

- 介电常数是表征电介质的最基本的参量。是衡量电介质在电场下的极化行为或储存电荷能力的参数。



(a)　(b)

电介质电容、介电常数（电容率）

- **真空电容**　$C_0=Q_0/V=\varepsilon_0 s/d$
- **电介质电容**　$C=Q/V=\varepsilon_r\varepsilon_0 s/d$
- **相对介电常数**　$\varepsilon_r = C / C_0$

Relative Permittivity

- The resultant capacitance can then be measured due to the dielectric:

  $C = \varepsilon_r A/d$

- the dielectric constant $\varepsilon_r = \varepsilon / \varepsilon_0$
- the dielectric constant, or relative permittivity, is the ratio of the permittivity of the material to the permittivity of free space ($\varepsilon_0 = 8.854 \times 10^{-12}$ F•m^{-1})

Dielectric Strength

- Very high electric fields (>10^8 V/m) can excite electrons to the conduction band and accelerate them to such high energies that they can, in turn, free other electrons, in an avalanche process (or electrical discharge). The field necessary to start the avalanche process is called dielectric strength or breakdown strength.
- The dielectric strength is a measure of how much voltage can be applied to a dielectric before electric current begins to arc across the dielectric.
- Arcing across the dielectric is known as dielectric breakdown.
- Dielectric strength has the units of V/m.

Dielectric Material

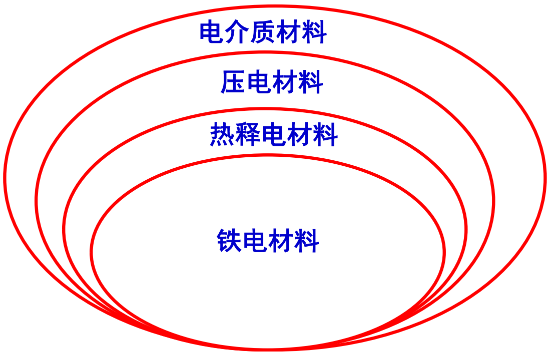
- **A dielectric material is a material that is nonmetallic and exhibits or may be made to exhibit an electric dipole structure.**
- **A dielectric material is characterized and selected according to its dielectric constant, Σr, often called the relative permittivity.**
- **There are many ceramics and polymers that exhibit dielectric behavior.**
- **Applications for dielectric materials**
  - **Dielectric materials to insulate electrical conductors**
  - **Dielectric materials used in capacitors**
  - **Communications (radio, radar and microwave)**
  - **Microelectronics**

32种点群-

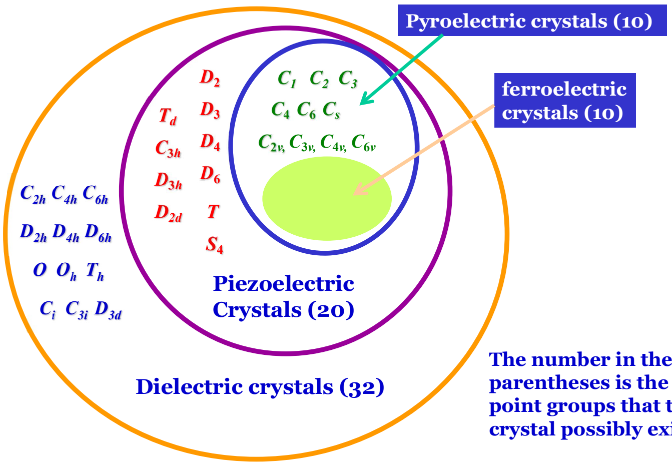
20个点群具有压电性

10个含单一对称轴，具有自发极化（热释电）

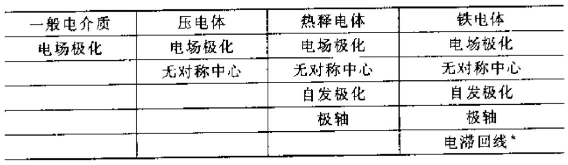
自发极化能被电场转向（铁电）



The Relations of Dielectric Crystals



The number in the parentheses is the point groups that the crystal possibly exist



一般电介质	压电体	热释电体	铁电体
电场极化	电场极化	电场极化	电场极化
	无对称中心	无对称中心	无对称中心
		自发极化	自发极化
		极轴	极轴
			电滞回线*

Piezoelectricity

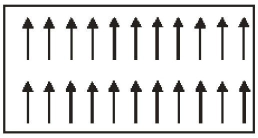
- In some ceramic materials, application of external forces produces an electric (polarization) field and vice-versa
- piezoelectric effect and converse piezoelectric effect: Some dielectrics have a crystal structure with one polar axis. Mechanical deformation of the crystal lattice causes electric displacement. On the other hand, the polar axis causes a deformation of the crystal lattice when electric charges are being displaced. This is called converse piezoelectric effect.
- Piezoelectric materials include barium titanate $BaTiO_3$, lead zirconate $PbZrO_3$, quartz.

Piezoelectricity

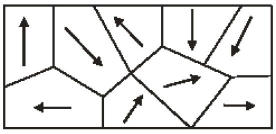
- The piezoelectric effect was first mentioned in 1817 by the French mineralogist Rene Just Hauy. It was first demonstrated by Pierre and Jacques Curie in 1880.
- The direct piezoelectric effect consists of the ability of certain crystalline materials (i.e. ceramics) to generate an electrical charge in proportion of an externally applied force.
- Applications of piezoelectric materials is based on conversion of mechanical strain into electricity (microphones, strain gauges et al.). The direct piezoelectric effect has been widely used in transducers design (accelerometers, force and pressure transducers ...).
- According to the inverse piezoelectric effect, an electric field induces a deformation of the piezoelectric material. The inverse piezoelectric effect has been applied in actuators design.

Piezoelectric Effect Basics

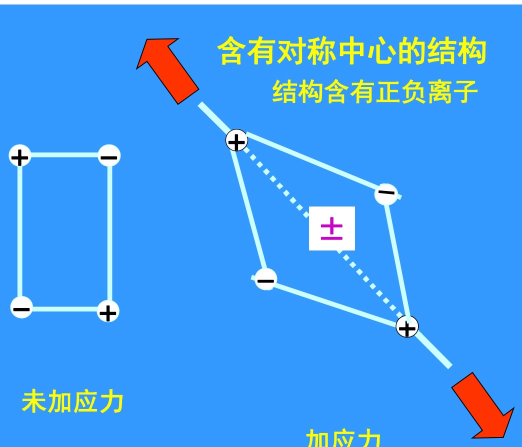
- Apply mechanical stress ⇒ Electric charge produced
- Apply electric field ⇒ Mechanical deformation produced
- Dipole: each molecule has a polarization, one end is more negatively charged and the other end is positively charged.
- Monocrystal: the polar axes of all of the dipoles lie in one direction. —— Symmetrical
- Polycrystal: there are different regions within the material that have a different polar axis. —— Asymmetrical



Monocrystal with single polar axis



Polycrystal with random polar axis



含有对称中心的结构

结构含有正负离子

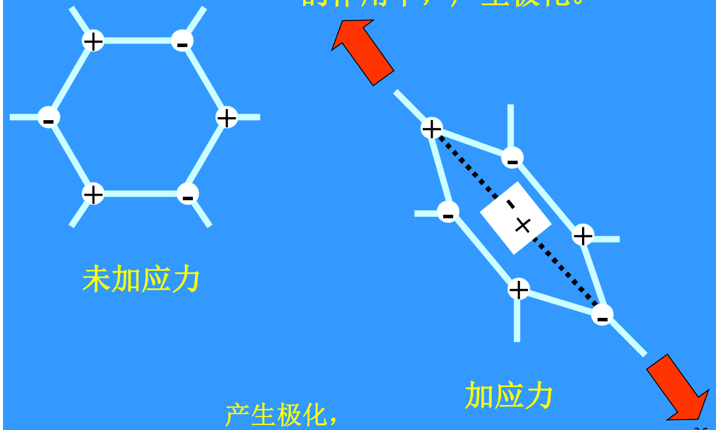
未加应力

加应力

正负电荷中心不分开，不产生极化

极化

压电--不具有自发极化特性，但为不对称中心结构，在外力的作用下，产生极化。



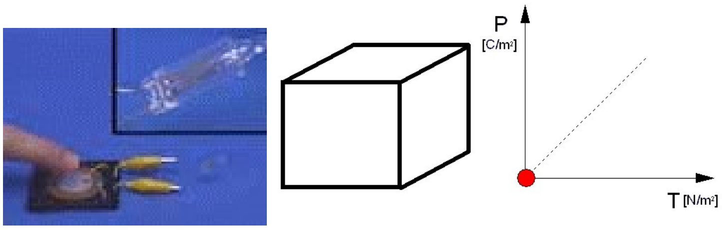
未加应力

加应力

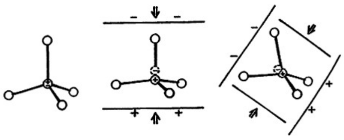
产生极化，
正负电荷中心分开

Piezoelectricity

- (Greek: piezo "to press")
- Some ionic crystals with polar axis show a piezoelectric effect.

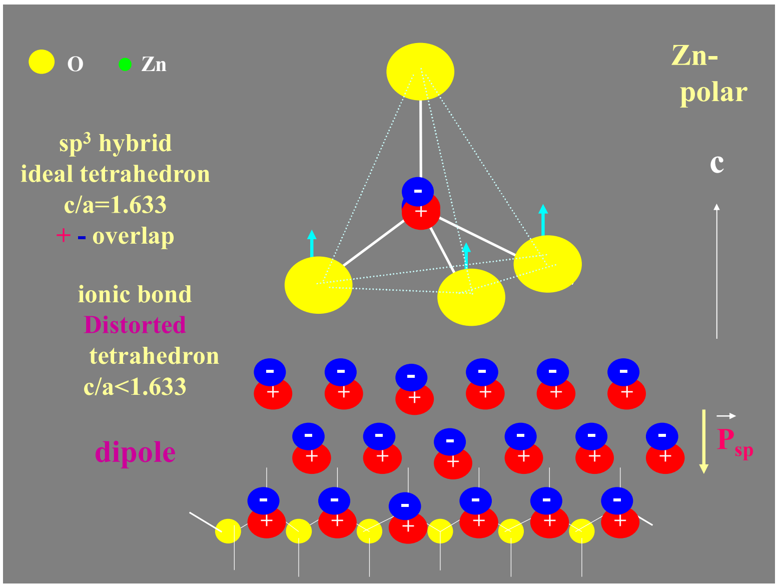


The Piezoelectric Effect vs Crystal Structure

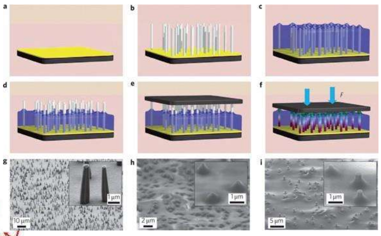


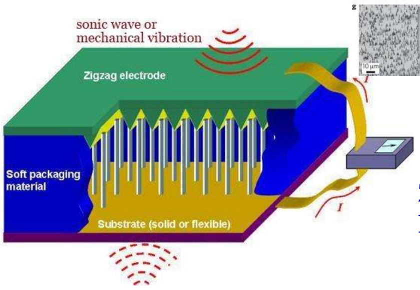
external pressure causes deformation and results in electric dipole

- If all tetrahedra have the same orientation or some other mutual orientation that does not allow for a compensation, then the action of all dipoles adds up and the whole crystal becomes a dipole.
- Two opposite faces of the crystal develop opposite electric charges.
- Crystals can only be piezoelectric if they are non-centrosymmetric.
- Sphalerite, Wurtzite ZnO, tourmaline, ammonium chloride and quartz are examples.



Piezoelectric Nanogenerators Based on Zinc Oxide Nanowire Arrays





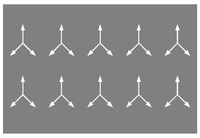
Self-powered nanowire devices

Zhong Lin Wang *et al*
Nature Nano 2010 5, 366

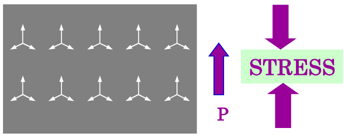
Zhong Lin Wang and Jinhui Song,
Science, 2006, 312: 242-246

Piezoelectricity

- Piezoelectric materials have crystal structures that lack inversion symmetry but show no spontaneous polarization
  ⇒ When the crystal is stressed however it develops a net polarization



in an unstressed piezoelectric crystal, the net polarization is equal to zero (arrows indicate the magnitude of the dipole moments along the three symmetry directions of the crystal)



application of stress to the crystal gives rise to a net polarization p

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Piezoelectricity

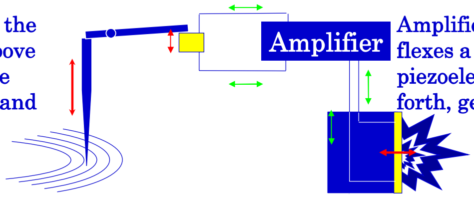
- Crystals where electrical polarization generated by mechanical stress —— in general, they are non-centrosymmetric.
- Strain shifts the relative positions of the positive and negative charges, giving rise to a net electric dipole.
- In 32 crystallographic point groups, 21 do not possess inversion symmetry elements, plus one cubic has a combination of symmetries, thus, only 20 groups can be piezoelectric.
- Many crystals with tetrahedral structure units (SiO_2, ZnO etc.),shearing stress causes distortional strain of tetrahedra.

Applications of Piezoelectric Crystals

- Mechanical to Electrical Conversion
  - Phonograph cartridges
  - Microphones
  - Vibration sensors
  - Accelerometers
  - Photoflash actuators
  - Gas igniters
  - Fuses

Piezoelectricity

Example: phonograph



Stylus motion squeezes a piezoelectric that in turn generates an electric current

Bumps in the record groove bounce the stylus up and down

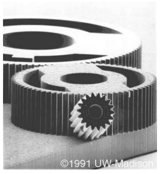
Amplified current flexes a second piezoelectric back and forth, generating sound

Applications of Piezoelectric Crystals

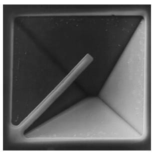
- Sensor technology
- force sensors
- Typical applications for piezoelectricity can be found in every household. One example are lighters. In this case a tiny prestressed hammer hits a piezoelectric material thus igniting a spark.

Gas and cigarette lighters

- Another area of application for dielectric materials is in micro-electro-mechanical systems (MEMS)
- Dielectrics are used to make microscopic gear structures for a range of applications
- In the transducer, stress exerted on some cantilever structure is converted into an electrical signal via the piezoelectric effect



microscopic gear wheels formed in PMMA (size scale is 100 mm!)



cantilever structure of width 10 mm and length 140 mm patterned in a silicon substrate

Applications of Piezoelectric Crystals

- **Electrical to Mechanical Conversion**
  - **Valves**
  - **Micropumps**
  - **Earphones and speakers**
  - **Ultrasonic cleaners**
  - **Emulsifiers**
  - **Sonic transducers**

Applications of Piezoelectric Crystals

- **Electrical-Mechanical-Electrical Conversion**
  - **Surface acoustic wave devices**
  - **Filters**
  - **Oscillators**
  - **Transformers**

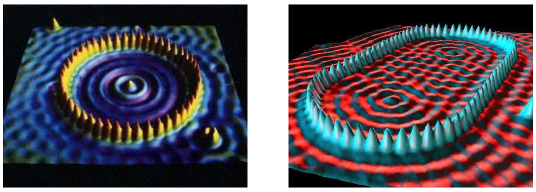
Quartz Crystal

Quartz is a piezoelectric material, meaning that it generates an electrical charge when mechanical pressure is applied. These crystals also vibrate when a voltage from an outside source, such as a battery, is applied. In the early 1920s W.G. Cady recognized that, due to their elastic qualities, mechanical strength and durability, quartz crystals could be used to fabricate very stable resonators. Cady also concluded that the crystal could be cut in specific ways that would create resonators of almost any frequency that were practically independent of temperature variations. Quartz crystals were first used as a time standard by Warren Marrison, who invented the first quartz clock in 1927. Juergen Staudte invented a method for mass-producing quartz crystals for watches in the early 1970s.

- **The frequency of the quartz oscillator is determined by the cut and shape of the quartz crystal.**
- **The quartz crystals inside watches today come in various shapes and frequencies. The most common crystals are miniature encapsulated tuning forks which vibrate 32,768 times per second. Other types of crystals vibrate at more than 50 million times per second.**
- **The oscillations of the balance wheel provide the time standard in mechanical timepieces.**
- **In contrast, in the history of mechanical watches, the balance wheel oscillated first at 2.5, then at 3, and finally at 5 cycles per second.**

Applications of Piezoelectricity

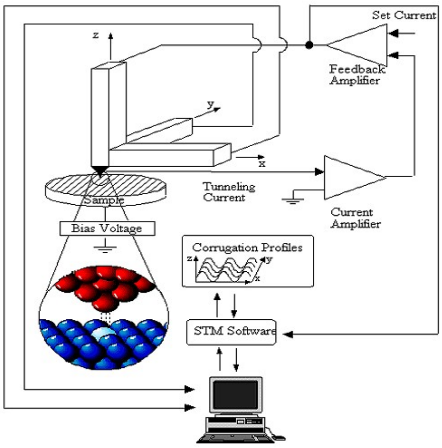
- **Piezoelectricity is exploited to convert electrical signals into sound in earphones**
- **Another important application is quartz resonators which may be used as frequency selective elements**
- **Piezoelectric materials such as PZT ($PbZrTiO_3$) are used to control the motion of the scanning tip in the scanning tunneling microscope (STM)**



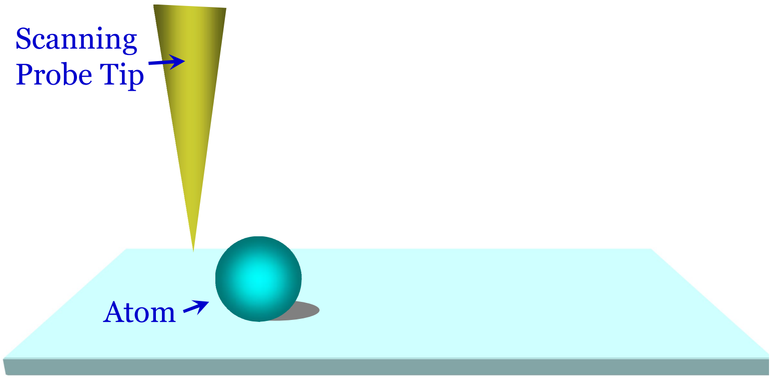
STM image of a corrals of atoms arranged using an STM

Scanning Tunneling Microscope

Ability to probe the geometric and electronic structure of a surface in-situ at the atomic level in real space.



Atomic Manipulation



Electrostriction （电致伸缩）

- **Electrostriction is a property of all electrical non-conductors, or dielectrics, that causes them to change their shape under the application of an electric field.**

- **Electrostriction is a property of all dielectric materials, and is caused by the presence of randomly-aligned electrical domains within the material. When an electric field is applied to the dielectric, the opposite sides of the domains become differently charged and attract each other, reducing material thickness in the direction of the applied field (and increasing thickness in the orthogonal directions). The resulting strain (ratio of deformation to the original dimension) is proportional to the square of the polarization. Reversal of the electric field does not reverse the direction of the deformation.**

Attention:

- **It should be noted that the related piezoelectric effect occurs only in a particular class of dielectrics. Electrostriction applies to all crystal symmetries, while the piezoelectric effect only applies to the 20 piezoelectric point groups. Electrostriction is a quadratic effect, unlike piezoelectricity, which is a linear effect.**

- **In addition, unlike piezoelectricity, electrostriction cannot be reversed: deformation will not induce an electric field.**

电致伸缩效应 *electrostrictive effect*

晶体在受到外电场E激励下产生形变S，但二者呈非线性关系，形变S与电场的平方E^2呈线性关系，即：

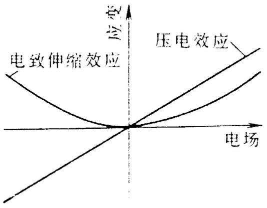
$$S \propto E^2$$

这种效应称为电致伸缩效应（电子云畸变）。

与压电效应的区别:

压电效应产生的应变与电场成正比，当电场反向时，应变改变符号，即正向电场使材料伸长，反向电场使材料缩短。

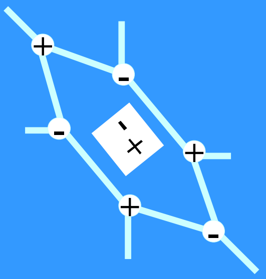
电致伸缩效应产生的应变与电场的平方成正比，当电场反向时，应变不改变符号，即无论正向电场或反向电场均使试样伸长（缩短）。



Pyroelectricity

- a subset where spontaneous polarization is caused by intrinsic internal strain accompanied by a lowering in symmetry to a different crystal structure.
- Pyroelectricity results from the temperature dependence of the spontaneous polarization of polar materials
- Pyroelectricity is the ability of certain materials to generate an electrical potential when they are heated or cooled. As a result of this change in temperature, positive and negative charges move to opposite ends through migration (i.e. the material becomes polarized) and hence, an electrical potential

热释电：在无应力和外电场存在的情况下也存在电极化，即自发极化。它们因受热产生电荷，故称为热释电体。



4、热释电效应 *pyroelectric effect*

本身具有自发极化，由于温度的变化，晶体出现结构上的电荷中心相对位移，使自发极化强度发生变化，从而在两端产生异号的束缚电荷，这种现象称为热释电效应。

The pyroelectric crystal classes:

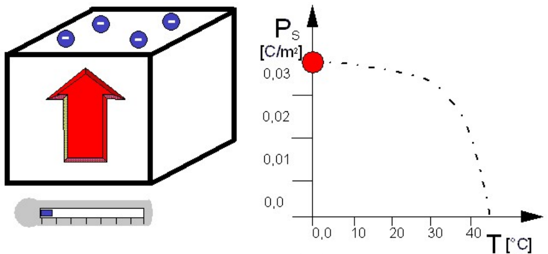
- Twenty of the 32 crystal classes are piezoelectric. All 20 piezoelectric classes lack a center of symmetry. Whether or not a material is polar is determined solely by its crystal structure. Only 10 of the 32 point groups are polar.
- All polar crystals are pyroelectric, so the 10 polar crystal classes are sometimes referred to as the pyroelectric classes.

10 point group:

$C_1, C_2, C_3, C_4, C_6, C_s, C_{2v}, C_{3v}, C_{4v}, C_{6v}$

Pyroelectricity

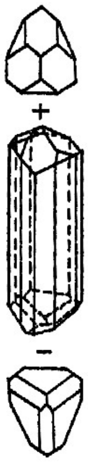
- Greek: pyro "to burn"
- Some piezoelectric crystals additionally show a pyroelectric effect.
- Pyroelectric materials possess a temperature dependent macroscopic electrical polarization.



Temperature dependence of the spontaneous polarization of triglycerin sulfate.

The ***pyroelectric effect*** in certain materials was recognized a long time ago, and such materials were referred as "*electric stones*". It was observed when such a stone was thrown in the fire, and it started to generate *electric charges* and caused a "cracking" sound. This is basically due to the ***temperature dependence of the spontaneous polarization*** of a *polar material*.

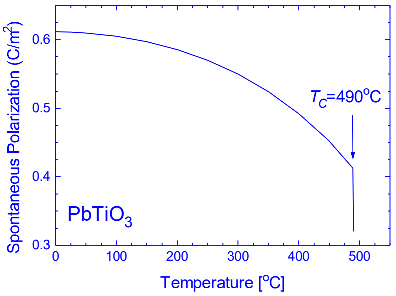
The Pyroelectric Effect of Tourmaline



Tourmaline : trigonal crystal, C_3 point group, have only 3-fold rotation axis. The pyroelectric effect happens on the direction of 3-fold rotation axis.

Examples: Pouring the mixture of sulfur powders (yellow) and PbO powders (red) through a sieve on a heated Tourmaline crystal. Due to the friction effect of the sieve, the PbO have positive charge and sulfur powders have negative charge, they will cover the two tops along the 3-fold rotation axis of Tourmaline crystal, indicating that heating makes the two tops of Tourmaline crystal have different charges along the 3-fold axis.

Pyroelectricity



The spontaneous polarization is strongly dependent on the temperature. It disappears completely at the phase transformation temperature T_C. The variation in the polarization with respect to the temperature is called the pyroelectric effect.

Examples for Application

- **Sensor technology**
- **motion detectors**
- **Pyroelectric materials are very sensitive! For instance thermal radiation of an human being is sufficient to create measurable electric voltage. This is widely used for commercial motion detectors.**

Motion detector

Practical applications of the *pyroelectric effect* in *temperature sensors* and *infrared light detectors* have been promoted.

The <u>merits</u> of pyrosensors as compared to semiconducting infrared-sensor materials are summarized as follows:

1). wide range of response frequency
2). use at room temperature
3). quick response in comparison with other temperature sensors
4). high quality materials for the pyrosensors are unnecessary

Heat Sensors

A temperature increase due to the *infrared irradiation* (such as human body) → *spontaneous polarization* → *variation in electric charge* (or *current*)

$\Delta T = \Delta H^* /(A_s h_1 \rho_o s_p)$

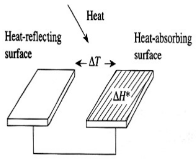
ΔH : the change in heat energy in J

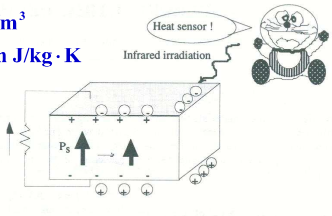
A_s : area of the slab in m^2

h_1 : thickness of the slab in m

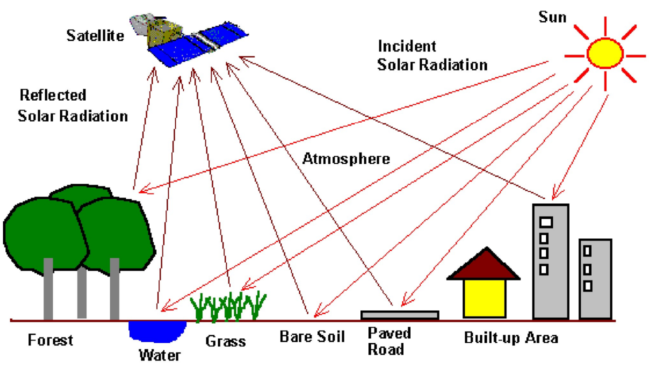
ρ_o : the density of the ferroelectric slab in kg/m^3

s_p : the specific heat of the ferroelectric slab in $J/kg \cdot K$

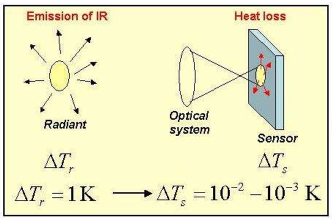


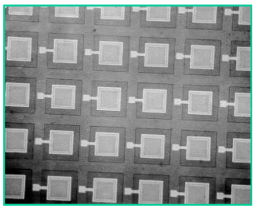


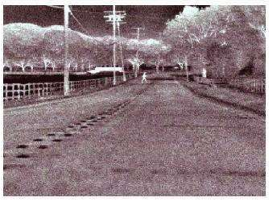
Infrared Image Sensors:

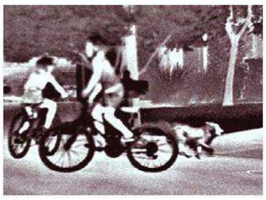


Pyroelectric Detectors/Sensors









Ferroelectrics

- **a subset of pyroelectrics**
- **electrical polarization can be reversed by the application of external electric field**
- **A pyroelectric crystal is also ferroelectric if the direction of the spontaneous polarization can be reversed under an applied electric field.**

铁电体的定义是指在某温度范围内具有自发极化且极化强度可以因外电场而反向的晶体。

铁电体的两个主要特点是：一是具有电滞回线，另一个是具有许多电畴。

铁电晶体内自发极化一致的区域称为电畴。铁电体中一般包含着多个电畴。两个相邻电畴自发极化间的夹角可以为180°或90°，分别称为180 °畴和90 °畴。

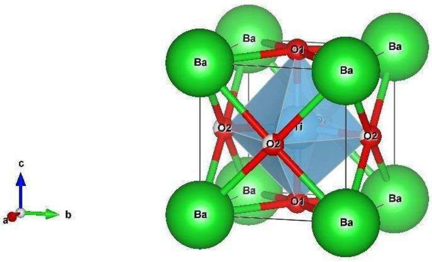
铁电性：在一定温度范围内具有自发极化，在外电场作用下，自发极化能重新取向，电位移矢量与电场强度间的关系呈电滞回线特征。

自发极化

$BaTiO_3$

钛酸钡的结构：

钙钛矿型结构



铁电体的位移性理论：

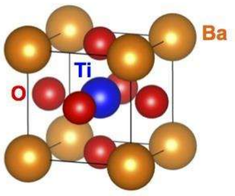
自发极化主要是由晶体中某些离子偏离了平衡位置，使单位晶胞中出现了偶极矩，偶极矩之间的相互作用使偏离平衡位置的离子在新的位置上稳定下来，同时晶体结构发生了畸变。

等轴晶系（大于120 °C）：

晶胞常数：a=4.01 A

氧离子的半径：1.32 A

钛离子的半径：　0.64 A



R+/R- = 0.485

钛离子处于氧八面体中，

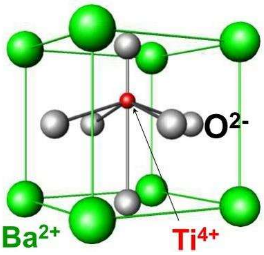
两个氧离子间的空隙为：4.01－2× 1.32= 1.37

钛离子的直径：2× 0.64= 1.28

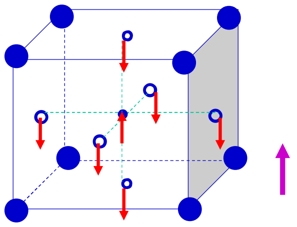
结果：

氧八面体空腔体积大于钛离子体积，给钛离子位移的余地。

较高温度时，热振动能比较大，钛离子难于在偏离中心的某一个位置上固定下来，接近六个氧离子的几率相等，晶体保持高的对称性，自发极化为零。



温度降低，钛离子平均热振动能降低，因热涨落，热振动能特别低的离子占很大比例，其能量不足以克服氧离子电场作用，有可能向某一个氧离子靠近，在新平衡位置上固定下来，并使这一氧离子出现强烈极化，发生自发极化，使晶体顺着这个方向延长，晶胞发生轻微畸变，由立方变为四方晶体。



固有偶极子

钛、氧离子的位移

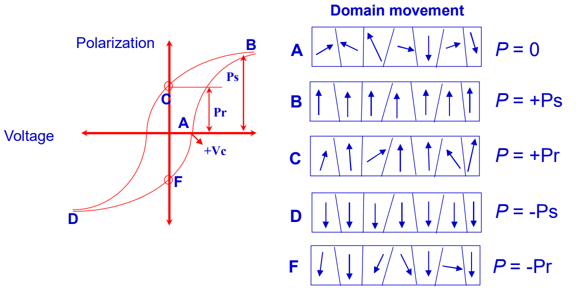
自发极化：这种极化状态并非由外电场引起，而是由晶体的内部结构引起。在这类晶体中，每一个晶胞内存在有固有电矩，通常将这类晶体称为极性晶体。

（一般介电极化，是介质在外电场作用下引起，没有外电场，这些介质的极化强度为0）

铁电体的主要特征

- 电滞回线 Hysteresis loop
- 电畴结构 Domain structure
- 居里温度 Curie temperature Tc
- 介电反常 Dielectric anomaly

Hysteresis vs. domain movement



- Domain : the region which has the same polarity
- Vc (Coercive Voltage) : the voltage where the net polarization is zero

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Ferroelectricity

- Ferroelectricity is a phenomena which was discovered in 1921.
- Ferroelectricity has also been called Seignette electricity, as Seignette or Rochelle Salt (RS) was the first material found to show ferroelectric properties.
- A huge leap in the research on ferroelectric materials came in the 1950's, leading to the widespread use of barium titanate ($BaTiO_3$) based ceramics in capacitor applications and piezoelectric transducer devices.

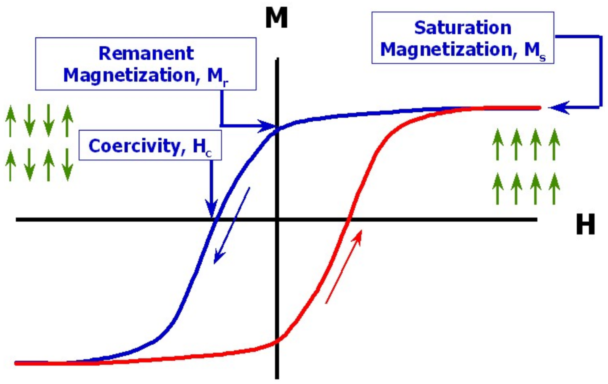
Ferroelectricity

- Pyroelectricity have a permanent net electric dipole in each primitive unit cell. e.g. ZnO is pyroelectric because ZnO_4 tetrahedra, each possessing a net dipole moment, all point in the same direction.
- Ferroelectric is a pyroelectric solid in which the spontaneous electrical polarization in a unit cell can be reversibly changed between $\pm P_s$, by application of and E field of suitable polarity.

Ferroelectricity

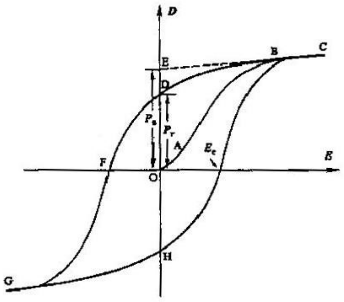
- Ferroelectricity derives its name from ferromagnetic.
- A magnetization can be observed that is reversible by applying a certain magnetic field.
- Ferroelectrics show a reversibility, but dealing with applied electric fields to reverse a material's polarization.

Magnetization Hysteresis Loop

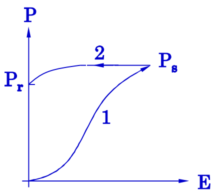


Ferroelectric Domains and Hysteresis Loop

- Ferroelectric crystals possess regions with uniform polarization called ferroelectric domains.
- Polarization vs. Electric Field (P–E) hysteresis loop for a typical ferroelectric crystal is shown on the right.



- The characteristic signature of ferroelectric crystals is the observation of hysteresis in their Polarization vs. Electric field curves.
- Prior to applying the electric field, the crystal is unpolarized since the permanent dipoles in the crystal are randomly oriented.
- However, with a strong applied electric field, the permanent dipoles polarize and saturation of the polarization is observed.
- When the field is then lowered back to zero, a remnant polarization then remains.

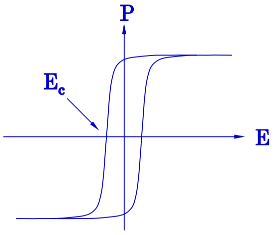


- Variation of polarization with electric field for a ferroelectric crystal below the curie temperature
- Starting from zero polarization at zero field, the electric field is increased and the polarization eventually saturates at the value p_s
- When the field is lowered back to zero, the polarization does not return to zero but exhibits a remnant polarization p_r

- With the ferroelectric crystal now polarized at zero field, it is necessary to apply a finite coercive field in the opposite direction to return the polarization to zero.
- If the reversed electric is then further increased beyond the coercive field, saturation of the polarization will occur again.

  ⇒ however, now the polarization will be oriented in the opposite direction to that obtained originally

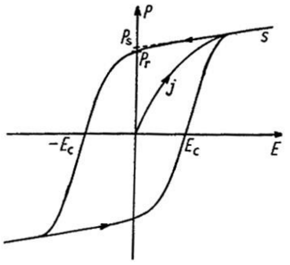
  ⇒ the polarization vs. electric field curve is therefore said to exhibit hysteresis



- the polarization-field curve of ferroelectric crystals typically shows hysteresis
- on the figure we indicate the coercive field E_c required to remove a net positive polarization in the crystal
- the area enclosed by the curve provides an indication of the energy dissipated by the field once a full cycle of the hysteresis loop has been achieved

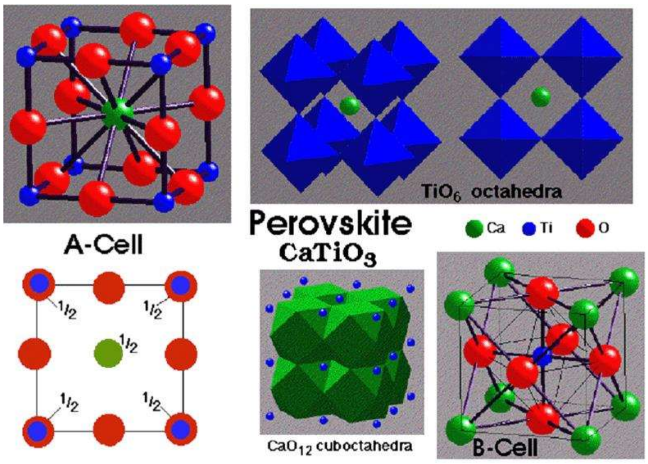
Hysteresis Loop

- curve s: when E is large enough, the whole crystal is one large domain
- when E is removed, a remnant polarization P_r remains, i.e. the crystal now is an electret.
- when a coercive field ($-E_c$) is applied, P_r can be removed. P_s is the spontaneous polarization corresponding to the polarization within a domain.
- No external E: the dipole moments of different domains compensate each other
- curve j: the total polarization of the crystal (if an increasing external electric field acts on the sample, those domains whose polarization corresponds to the direction of the electric field will grow at the expense of the remaining domains).

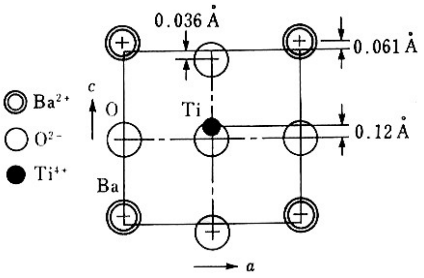


Atomic Arrangement and Ferroelectricity

- The arrangement of the atoms in all ferroelectric crystals result in an equally stable state but with reoriented Ps.
- A simple example is $BaTiO_3$ for which the prototype is cubic.
- The paraelectric to ferroelectric transformation at Tc may be viewed in terms of a low-frequency temperature-dependent mode of the crystal lattice, observable by optical or neutron spectroscopy.



Barium Titanate

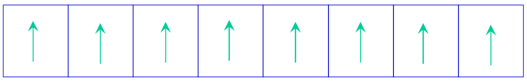


•Barium Titanate ($BaTiO_3$) — the first material to be developed as a ferroceramic
•available in single crystal form
•The absence of center symmetry in crystal structure gives rise to spontaneous polarization
•Cubic above Curie temperature; tetragonal as it cools down

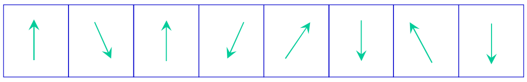
Ferroelectric Transitions

⌗Curie Temperature, T_c: transition from randomized paraelectric and ordered ferroelectric phase.

Ferroelectric



Paraelectric



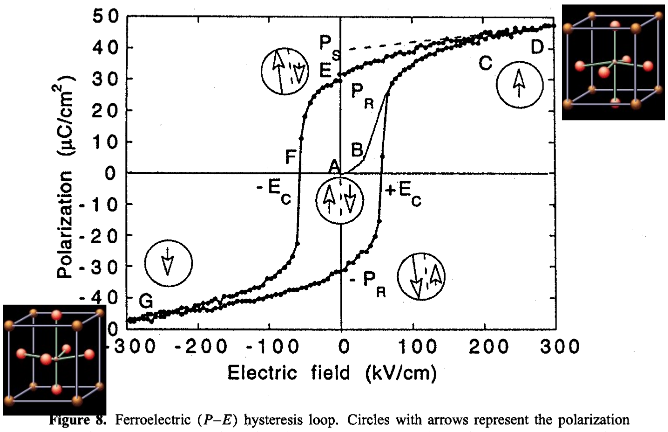


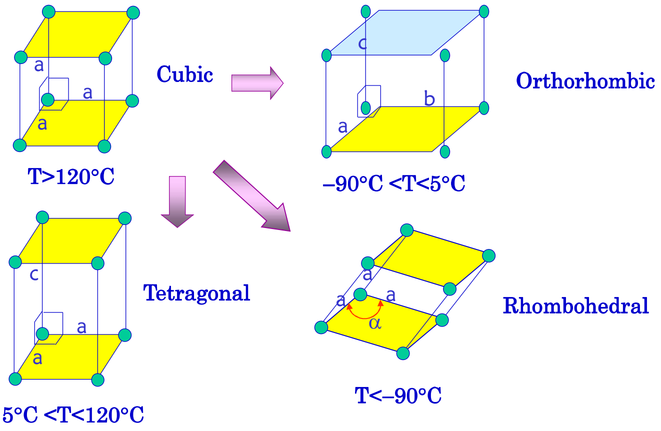
Figure 8. Ferroelectric (P–E) hysteresis loop. Circles with arrows represent the polarization state of the material at the indicated fields. The symbols are explained in the text. The actual loop is measured on a (111)-oriented 1.3 μm thick sol-gel $Pb(Zr_{0.45}Ti_{0.55})O_3$ film. (Experimental data courtesy of D V Taylor.)

Ferroelectricity

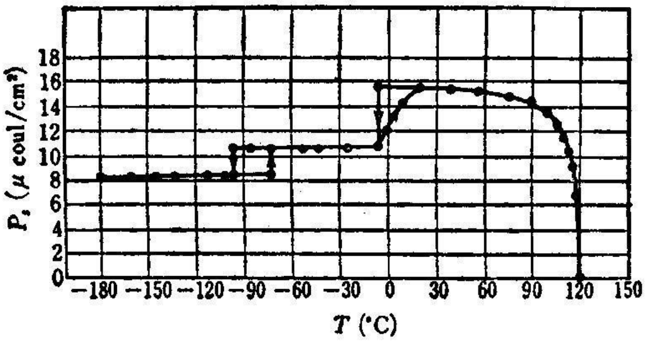
⌖Previously we saw that dielectric crystals develop a net polarization in the presence of an applied electric field.
⌖In certain crystals known as ferroelectrics, however, the polarization can persist when the applied electric field is removed!
⌖Ferroelectric behavior is only observed below a critical temperature known as the Curie temperature T_C
⇒ At temperatures above this, normal dielectric behavior is obtained

MATERIAL	T_C (K)	Ps (μCcm^{-2})
$BaTiO_3$	408	26.0
$SrTiO_3$	110	
$KNbO_3$	708	30.0
$PbTiO_3$	765	>50
$LaTaO_3$	938	50
$LiNbO_3$	1480	71
GeTe	670	

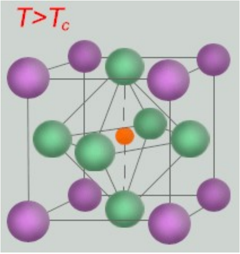
Temperature Dependence of Barium Titanate Crystal Structure

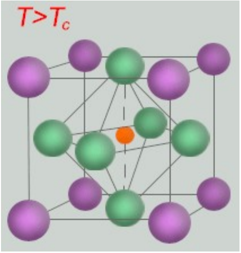


Spontaneous polarization of $BaTiO_3$



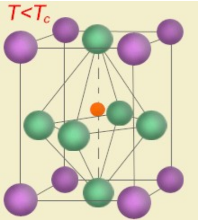
- At a microscopic level, ferroelectrics can be understood to be those materials whose crystal structures contain charged ions that are displaced from high-symmetry points.
- This displacement in turn gives rise to a net polarization of the crystal unit cell.
- A good example of a ferroelectric crystal is barium titanate ($BaTiO_3$) which features two positively-charged ions and one negatively-charged ion.
- Above the Curie temperature, these ions are distributed in a perovskite crystal structure and the crystal behaves as a normal dielectric with no spontaneous polarization.





- crystal structure of barium titanate at temperatures above the Curie temperature
- in this crystal configuration there is no net polarization of the unit cell and the crystal behaves as a normal dielectric
- at temperatures above the curie temperature ferroelectric materials are said to be paraelectric

- As the temperature is lowered below the curie temperature, the crystal structure deforms and the unit cell develops a net dipole moment along the vertical axis of the unit cell.
- In the ferroelectric state, a large number of dipoles align to form ferroelectric domains that are typically randomly oriented at zero field.
- An electric field may be used to align the domains with respect to each other.



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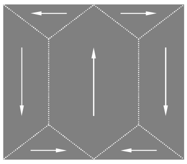
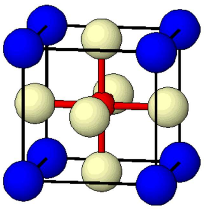


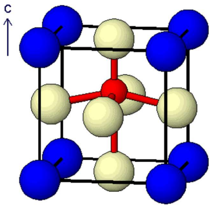
random alignment of the dipoles of different domains in a ferroelectric crystal with no applied electric field

In $SrTiO_3$, Ti–O~1.95Å
a typical bond length for Ti-O;
stable as a cubic structure →

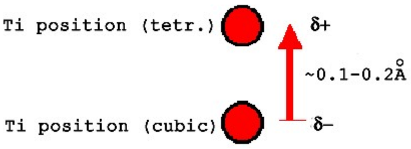


↓ larger

In $BaTiO_3$, Ti–O is stretched, >2.0Å. Too long for a stable structure.
Ti displaces off its central position towards one oxygen
→ square pyramidal coordination →



This creates a net dipole moment:



- Displacement by 5–10% Ti–O bond length

- Random dipole orientations paraelectric
- Aligned dipole orientations ferroelectric

- Under an applied electric field, dipole orientations can be reversed, i.e. the structure is polarizable.

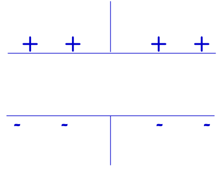
- Dipoles tend to be 'frozen in' at room temperature; as increase temperature, thermal vibrations increase the polarizability

Dimensionality of Ferroelectric Crystals

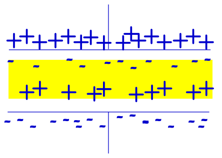
- **one-dimensional, $BaTiO_3$: $P_s > 25 \times 10^{-2}$ C m^{-2}**
- **two-dimensional, $BaCoF_4$: P_s between 10×10^{-2} and 3×10^{-2} C m^{-2}**
- **three dimensions, $Tb_2(MoO_4)_3$: $P_s < 5 \times 10^{-2}$ C m^{-2}**

Ferroelectricity

Ferroelectric materials exhibit spontaneous polarization. This polarization can be aligned by an electric field, and will remain aligned even after the field is removed. It occurs from the nonsymmetric shape of the complex ferroelectric's unit cell. Ferroelectrics are principally used to improve the performance of capacitors.



Normal Capacitor

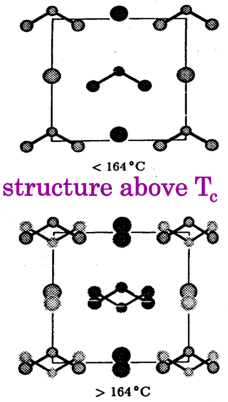


Ferroelectric Capacitor

Ferroelectric Crystal of $NaNO_2$

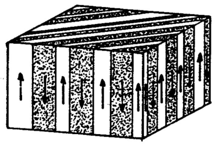
structure below T_c

structure above T_c



paraelectirc form

macroscopic dipole moment in ferroelectirc form



In sodium nitrite the ferroelectric polarization only occurs in one direction.

Applications of Ferroelectricity

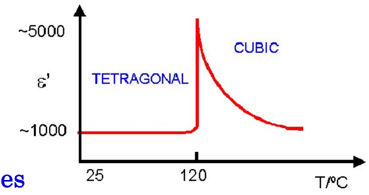
Ferroelectric materials have a number of different applications in technology:

- The hysteresis curve that these materials exhibit can be utilized for memory devices in computers
- The dielectric constant of ferroelectrics is orders of magnitude larger than that of normal dielectrics ⇒ They may therefore be used as dielectric materials in ultra-compact and high-efficiency capacitors
- The dielectric constant and so the refractive index of these materials may be tuned by varying an external electric field ⇒ this allows the use of these materials as optical switches

Define the permittivity or dielectric constant of a material by:

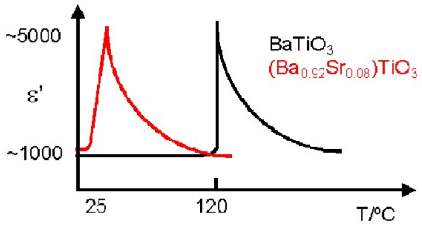
$$\varepsilon' = \frac{Q}{Q_{vac}}$$

- H_2O is a polar liquid: ε ~80
- Typical ionic solids: ε ~10
- Air: ε ~1
- $BaTiO_3$:
  - Below 120°C, $BaTiO_3$ is ferroelectric with aligned dipoles. Residual dipole disorder gives ε ~200-1000
  - At~120°C, tetragonal → cubic phase transition. Dipoles randomize and ε increases to ~5,000-10,000

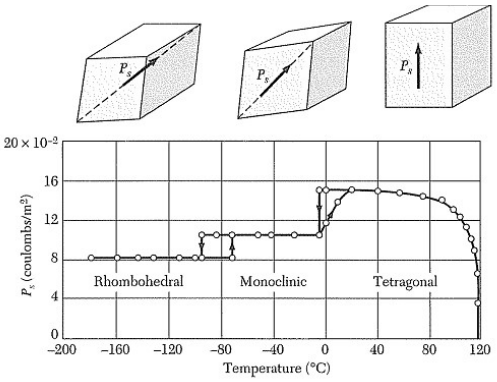


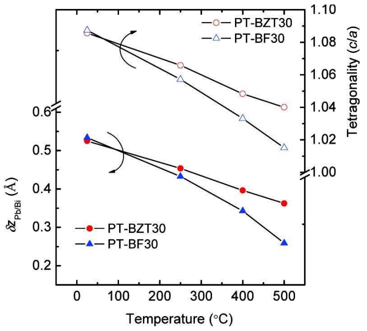
- For capacitor applications, need to increase capacitance [energy stored/mass or volume] by increasing Q and thus increasing ε′
- How to do this? $BaTiO_3$ is very good at 120°C but want high ε′ at room temperature!

Solution: Partial substitution of Ba by a smaller M^{2+} ion - Sr^{2+} ; unit cell volume decreases and the phase transition temperature decreases



Polarization vs Ferroelectricity





Tetragonality (*c*/*a*) and *P*S displacement of Pb/Bi (δzPb/Bi) in PT−BZT30 and PT−BF30 as functions of temperature.