MME2045 BLOCK F - Functional Materials

Functional materials find a wide range of important technical applications. In this Block we will cover a number of functional materials relevant to mechanical applications including energy materials for fuel cells, rechargeable batteries, supercapacitors; ferromagnetic materials; and piezoelectric materials. This notes lists the key knowledge points on ferromagnetic materials, and dielectric, ferroelectric, piezoelectric and pyroelectric materials.

1. Ferromagnetic Materials

1.1 Quantity and Symbols

The magnetic field strength (**H**) and magnetic flux density (**B**) are related according to:

B = μH   (1)

The parameter **μ** is called **permeability**.

In a vacuum: **B_0 = $μ_0$H**   (2)

Where **$μ_0$** is the permeability of a vacuum (**$μ_0$= $4π×10^{-7}$ H/m**).

Relative permeability: **$μ_r$ = $μ/μ_0$**   (3)

The total flux density associated with a field H with a magnetic material is:

B = $μ_0$(H + M)   (4)

M is called the magnetisation = **M = χH**   (5)

M is the magnetisation of the magnetic material. So the total flux density B is due to both the magnetising field strength H (which gives $μ_0$H) and to the magnetisation of the material M (which gives $μ_0$M).

B = $μ_0μ_r$H = $μ_0$(H + M)   (6)

So **$μ_r$H = H + M**   (7)

M= ($μ_r$ − 1) H   (8)

Magnetic **susceptibility χ = $μ_r$ − 1**   (9)

1.2 The five magnetic behaviours of materials

The magnetic behaviours of materials can be classified into the following five groups:

Paramagnetism – a very weak form of magnetism. χ is positive and is typically in the order of 10^{-5} – 10^{-3}. In the absence of an external magnetic field, the magnetic moments are randomly oriented, and the net magnetic moment is zero. When an external magnetic field is applied, these magnetic moments will tend to align themselves in the same direction as the applied field, thus producing a

positive magnetisation and reinforcing magnetic flux density (only very slightly). The induced magnetisation becomes zero when the magnetic field is removed.

Diamagnetism – a very weak form of magnetism. χ is negative and is typically in the order of -10^{-6} – -10^{-5}. The net magnetic moment is zero when there is no external magnetic field. When an external magnetic field is applied, magnetic moments align in a direction opposite to that of the applied field, thus producing a negative magnetisation and reducing the total magnetic flux density (only very slightly). The induced magnetisation becomes zero when the magnetic field is removed.

Paramagnetism and diamagnetism are the two most common types of magnetism, accounting for most of the elements in the periodic table at room temperature.

Ferromagnetism – Ferromagnetic materials have unpaired electrons. Very large permanent magnetic moments can exist in the absence of an external magnetic field. Initially, the magnetic moments can be randomly oriented. When an external field is applied, giant magnetisation can be produced. Once the external magnetic field is removed, some of the induced magnetisation retains.

Only very few elements in the periodic table exhibit ferromagnetism. Fe, Ni, Co and some rare earth elements (such as neodymium) and their alloys are the typical ferromagnetic materials and are used to make permanent magnets.

Antiferromagnetism - the intrinsic magnetic moments of neighbouring valence electrons to point in opposite directions. Thus, the magnetic moments cancels out each other.

Ferrimagnetism - neighbouring pairs of electron spins point in opposite directions. BUT there is more magnetic moment from the sub lattice of electrons that point in one direction, than the other. Typical in oxides. The produced magnetisation is large enough to be of commercial value but their magnetic saturation is not as high as that of ferromagnetic materials.

Table 1. Different types of magnetic behaviours

type	spin alignment	spin in simplified plot	examples
ferromagnetic	all spins align parallel to one another: spontaneous magnetization- $M = a + b$		Fe, Co, Ni, Gd, Dy, $SmCo_5$, Sm_2Co_{17}, $Nd_2Fe_{14}B$
ferrimagnetic	most spins parallel to one another, some spins antiparallel: spontaneous magnetization- $M = a - b > 0$		magnetite (Fe_3O_4), yttrium iron garnet (YIG), $GdCo_5$
antiferromagnetic	periodic parallel-antiparallel spin distribution: $M = a - b = 0$		chromium, FeMn, NiO
paramagnetic	spins tend to align parallel to an external magnetic field: $M = 0$ @ $H=0$, $M > 0$ @ $H > 0$		oxygen, sodium, aluminum, calcium, uranium
diamagnetic	spins tend to align antiparallel to an external magnetic field $M = 0$ @ $H=0$, $M < 0$ @ $H > 0$		superconductors, nitrogen, copper, silver, gold, water, organic compounds

1.3 Magnetic hysteresis loop (B-H loop and M-H loop)
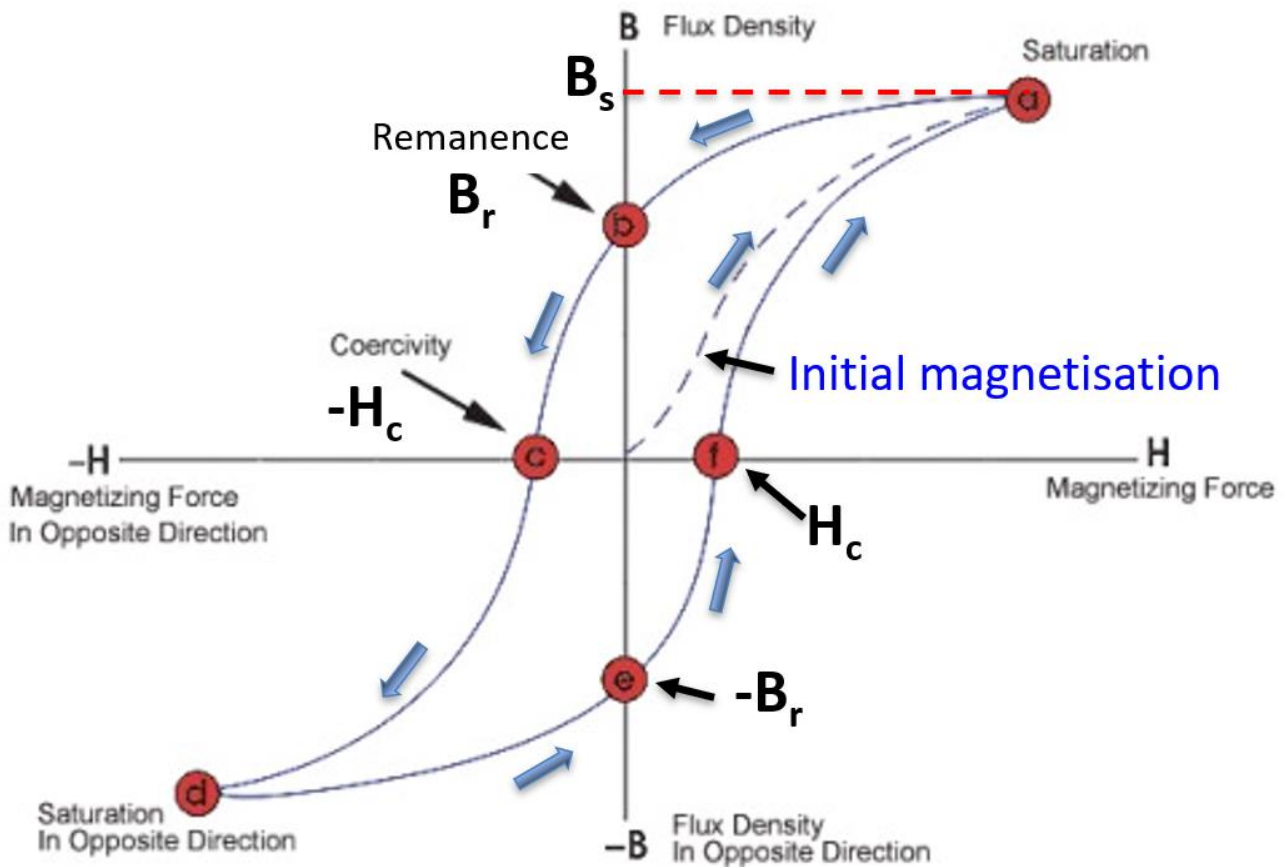

Figure 1. Magnetic hysteresis loop (B-H loop).

Point **a**: **saturation magnetic flux density, B_s**. When the magnetic field strength H increases from zero, magnetic flux density B increases until reaching point **a**, the maximum contribution to the magnetic flux density from the material under an external magnetic field - in which all atomic moments maximally aligned.

Point **b**: **remanent magnetisation B_r**. If external magnetic field strength H is reduced to zero, residual magnetism is still present.

Point **c**: **Coercivity H_c**. To reduce flux density B to zero, a magnetic field in the direction opposite to that of original field.

Point **d**: by further increasing the magnetic field in opposite direction, saturation is achieved in opposite direction.

Point **e**: negative B_r with reducing magnetic field to zero.
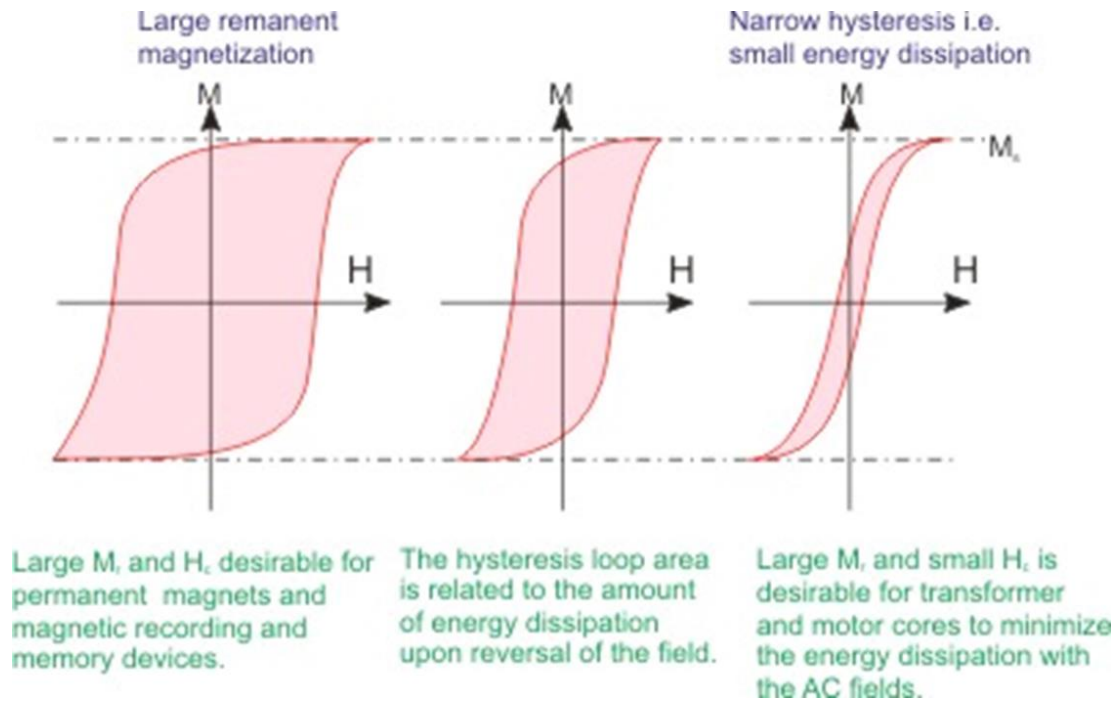
Point **f:** Coercivity H_c.

Large remanent magnetization

M ... H

Narrow hysteresis i.e. small energy dissipation

M ... H ... M ... H ... M_s

Large M_r and H_c desirable for permanent magnets and magnetic recording and memory devices.

The hysteresis loop area is related to the amount of energy dissipation upon reversal of the field.

Large M_r and small H_c is desirable for transformer and motor cores to minimize the energy dissipation with the AC fields.

Figure 2. M-H loops with different H_c.

In addition to B-H loops, often M-H loops are also plotted. Note that $B = \mu H$ and $M = (\mu_r - 1) H$.

In M-H loops, M represents just the magnetisation of the material as a function of external magnetising field strength H.

1.4 Maximum Energy Product: BH_{max}

$B_d \times H_d < (BH)_{max}$
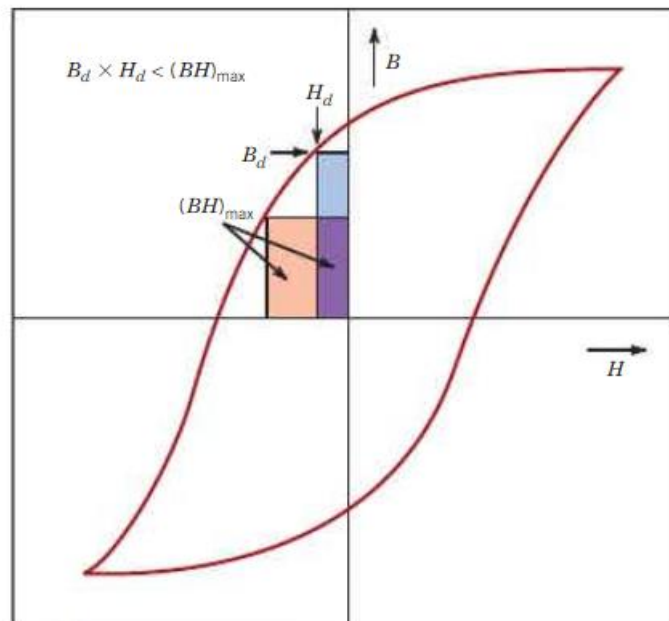
H_d

B_d

$(BH)_{max}$

B

H

Figure 3. Maximum Energy Product: $(BH)_{max}$ (William D. Callister Jr., David G. Rethwisch. Materials Science and Engineering).

The product of H and B is called the energy product. The maximum value of this product (the area of the largest B-H rectangle in the second quadrant in the B-H loop) is the maximum energy product.

$(BH)_{max}$ is a frequently used merit index for permanent magnetic materials indicating capacity to support external fields.

$(BH)_{max}$ is a measure of the maximum amount of useful work that can be performed by the magnet. Designs that operate at $(BH)_{max}$ make best use of available magnetic energy.
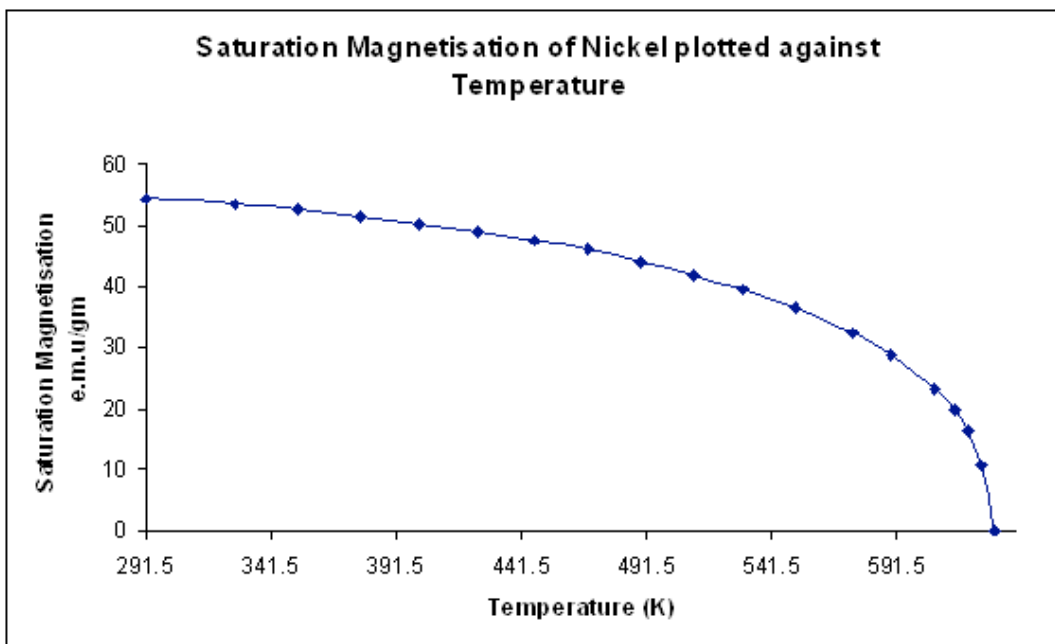
1.5 Curie Temperature (T_c)

Figure 4. The saturation magnetisation of Ni as a function of temperature.

The induced magnetisation typically decreases with increasing temperature. Curie Temperature (T_c) is the temperature above which the ferromagnetic characteristic is lost, and the ferromagnetic material becomes paramagnetic. Higher Tc is typically desired for practical applications.

1.6 Hard and soft magnets

Ferromagnetic materials are divided into two groups depending on their coercivity (H_c).

Soft magnets have low coercivity, typically less than 1,000 A/m. Such materials can be easily magnetised and demagnetised. Soft magnets have thin B-H (M-H) loops.

The energy loss during magnetising and demagnetising processes is proportional to the area of the B-H hysteresis loop. Soft magnets with a very narrow hysteresis loop are needed in applications where rapid changes in the magnetisation during operation occur (e.g., transformer cores) to reduce energy loss.

5

High electrical resistivity is also desirable to reduce eddy current loss.

Large saturation flux density B_s (high permeability μ_r or high susceptibility χ) is desired to keep device volume down.

Hard magnets have high coercivity, typically in the order of 10^4 - 10^6 A/m. Once magnetised, hard magnets are not easily demagnetised. Hard magnets have large B-H (M-H) loops.

Hard magnets are used where the high coercivity allows them to retain the magnetisation state once magnetised such as applications for dc electric motors. For permanent magnet motors applications, high remanence (B_r) coercivity (H_c) and $(BH)_{max}$ are required.

2. Dielectric, Ferroelectric, Piezoelectric and Pyroelectric Materials

2.1 Quantity and Symbols

Capacitance of a dielectric is given by Equation 10:

C = εA/d (10)

In vacuum,

$$C_0 = \varepsilon_0 A/d \tag{11}$$

Where **ε** is the permittivity of the dielectric material, **ε_0** is vacuum permittivity (a constant, 8.854×10^{-12} F/m), **A** is area and d is thickness of a capacitor.

Comparison of the two capacitances, C/C_o, results in a relationship called **relative permittivity or dielectric constant, ε_r**.

$\varepsilon_r = (\varepsilon A/d)/(\varepsilon_0 A/d) = \varepsilon/\varepsilon_o$

The dielectric constant, or relative permittivity, is the ratio of the permittivity of the material to the permittivity of vacuum. The relative permittivity is directly proportional to the capacitance.

Electric flux density D [C/m^2]: $D = \varepsilon_0 E + P = \varepsilon E$ (12)

Electric susceptibility χ [no units]: $\chi = P/(\varepsilon_0 E)$ (13)

$= (\varepsilon_r \varepsilon_0 E - \varepsilon_o E)/(\varepsilon_0 E) = \varepsilon_r - 1$ (14)

where D is the electric flux density, which is related to the electric field (E) by $D = \varepsilon E$.

$\varepsilon_0 E$ is the flux component due to the applied electric field and P (polarisation) is flux component due to dipoles present in the dielectric material.

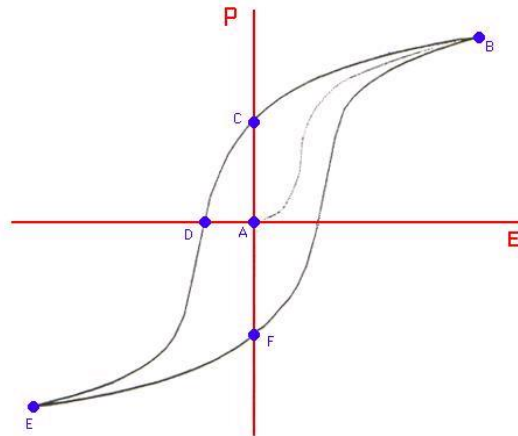## 2.2 Polarisation-electric field (P-E) hysteresis loop

Figure 5. Polarisation-electric field (P-E) hysteresis loop of a ferroelectric material.

Ferroelectrics exhibit spontaneous polarisation that can be reversed by the application of an electric field. The polarisation-electric field (P-E) hysteresis loop of a ferroelectric material looks similar to that of the B-H (M-H) loop for a ferromagnetic material.

Point **A**: with no electric field applied the dipoles are in a random order and no polarisation is found.

Point **B**: **saturation polarisation (P_s).** If a positive external electric field is now applied, polarisation increase with increasing the applied field. When this point is at a maximum, saturation polarisation results and a majority of the dipoles are aligned with the applied field.

Point **C**: **remanent polarisation (P_r).** After the electric field is removed, the polarisation decreases to a remenant polarisation. This results from the oriented dipoles being unable to return to their original random state without an additional energy input by an oppositely directed field.

Point **D**: **coercive field (E_c)**. The strength of the electric field required to return the polarisation to zero is known as the coercive field -E_c.

Point **E**: Decreasing this electric field further will lead to saturation polarisation.

Point **F**: Once again, when the field is removed, a negative remnant polarisation occurs.

2.3 Curie temperature T_c

Ferroelectric materials exhibit spontaneous polarisation below their **Curie temperature T_c**. The polarisation typically deceases with increasing temperature. Above T_c ferroelectricity disappears and the material becomes paraelectric.
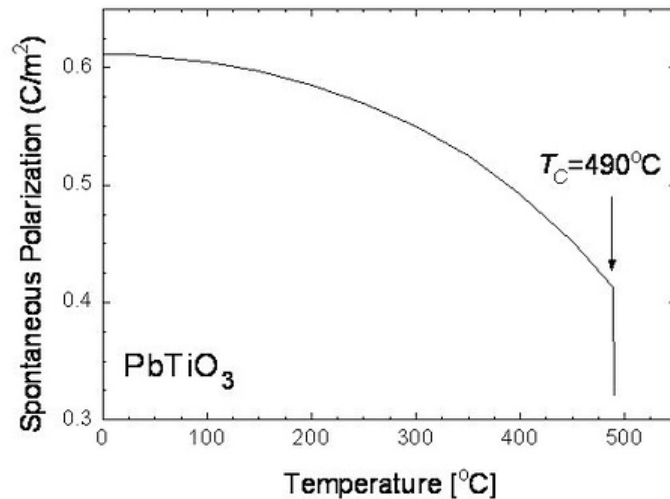
Figure 6. Polarisation of $PbTiO_3$ as a function of temperature.

2.4 Ferroelectric materials and applications

Barium titanate ($BaTiO_3$) is the most commonly used ferroelectric material mainly due to its giant relative permittivity. The giant relative permittivity is associated with the crystal structure of $BaTiO_3$ (it adopts a perovskite-type structure), in which the titanium atoms can move from their positions.

The giant relative permittivity can be used to make ferroelectric multilayer ceramic capacitors (MLCC) which are required in modern electronic devices. Note that $C = \varepsilon A/d = \varepsilon_0 \varepsilon_r A/d$. So a giant relative permittivity ε_r can give high capacitance.

2.5 Piezoelectric materials and applications

Piezoelectric effect

Direct piezoelectric effect: a force generates an electric field (voltage/current) that can be amplified and is proportional to strain or pressure.

Inverse piezoelectric effect: an applied electric field generates deformation that can be used to create a displacement or force.

Wide range of applications

❖ generators (e.g. gas igniters)

❖ sensors (e.g. accelerometers, pressure sensors)

❖ ultrasonic transducers (e.g. in medical imaging, sonar)

❖ actuators (for diesel fuel injectors, micropositioning, micropumps, microvalves)

❖ speakers, buzzers (e.g. in mobile phones)
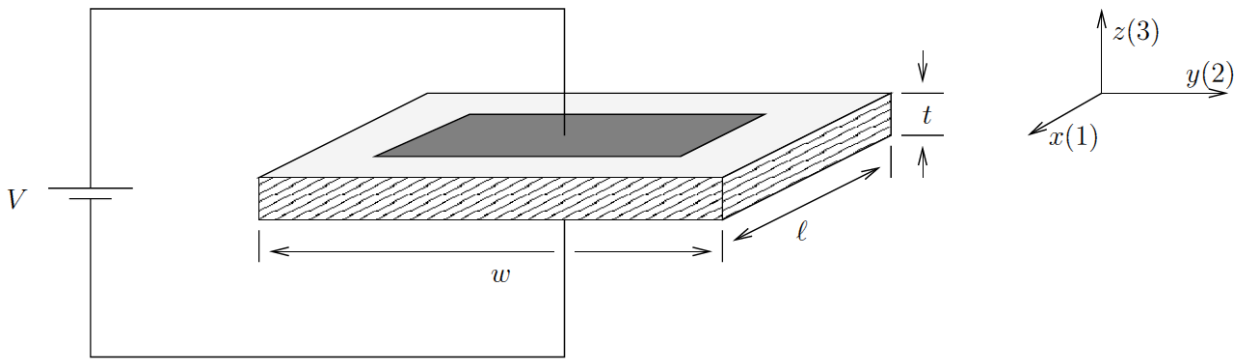
❖ quartz oscillators (e.g. for timing in microelectronics)

8

Figure 7. A piezoelectric transducer arrangement for piezoelectric coefficient measurement

The piezoelectric coefficient d_{ij} is the ratio of the strain in the j-axis to the electric field applied along the i-axis, when all external stresses are held constant. When a voltage is applied across the thickness of the piezoelectric materials, the dimensional changes can be calculated using the equations below.

$$\Delta l = d_{31} \times V \times (l/t)$$

$$\Delta w = d_{31} \times V \times (w/t)$$

$$\Delta t = d_{33} \times V$$

The dimensional changes are small and are typically in the order of **nm-μm**.

Lead zirconate titanate with the chemical formula $Pb[Zr_xTi_{1-x}]O_3$ ($0 \leq x \leq 1$, PZT) is most commonly used today for piezoelectric applications. PZT adopts a perovskite structure similar to that of $BaTiO_3$.

PZT are classified as '**soft**' or '**hard**' according to the **coercive field (E_c)**. Hard PZT materials have **high E_c** whereas soft PZT materials have **low E_c**.

2.6 Pyroelectric effect

The polarisation in dielectric materials is temperature dependent. This leads to the pyroelectric effect which enables the conversion of radiant heat energy into electrical signals.

A passive Infrared (PIR) sensor can detect the infrared light radiated by a warm object. It consists of pyroelectric sensors which convert changes in their temperature (due to incident infrared radiation) into electric signal. Pyroelectric sensors are very sensitive to temperature and can detect temperature changes from surroundings to as little as 10^{-6} K.