

PROPERTIES OF CERAMIC MATERIALS

4.1 Introduction

The use of ceramic materials in different applications is based on the understanding of their properties. In this chapter are reviewed the main aspects of such properties as thermal, mechanical, electrical, magnetic and optical properties. This coverage is far from complete and the additional reading material mentioned at the end of the chapter offers more details.

4.2 Thermal properties

4.2.1 Thermal expansion

The linear thermal expansion coefficient of a material is defined as the rate of change of its length (L) with respect to temperature (T) per unit initial length (L_0).

$$\alpha = \frac{1}{L_0} \frac{dL}{dT} \quad \text{K}^{-1} \quad (4.1)$$

The thermal expansion of a material is caused by the vibrations of the atoms (or ions) about their equilibrium positions which cause lengthening of bonds. The linear coefficients of expansion of some common ceramic materials are listed in Table (4.1)

Table 4.1: Linear coefficient of expansion of some ceramic materials

Material	Al ₂ O ₃	BeO	MgO	TiO ₂	AlN	SiC	Glass	Pyrex	Porcelain
$\alpha \times 10^6 \text{ K}^{-1}$	8 - 9	8.5-9	13.5	8.5	5.6	4.5	9	3.2	4.3

It is clear from the previous table that the values of the thermal coefficients of expansion of ceramics are in the range $\sim 10^{-6} \text{ K}^{-1}$. These values are generally lower than those of metals. For example, the value of α for aluminum is $2.35 \times 10^{-5} \text{ K}^{-1}$. For zinc, it is $6.43 \times 10^{-5} \text{ K}^{-1}$. These values are one order of magnitude greater than those of ceramics.

Another feature is that the thermal coefficient of expansion is higher for ionic than for covalent solids (for example, compare MgO and SiC). The reason is that covalent ceramics have more open structures than most ionic ceramics. In closed packed structures, all the vibrations caused by the input thermal energy contribute to expansion. On the other hand, in covalent materials, part only of the thermal vibrations contributes to lengthening of bonds, which is responsible for expansion. Another part causes a change in bonds angles, which is not associated with any expansion.

Also, the thermal coefficient of expansion increases with temperature. For example, its average value for silica glass is $5.7 \times 10^{-6} \text{ K}^{-1}$ over the temperature range $20 - 500^\circ\text{C}$, and $6 \times 10^{-5} \text{ K}^{-1}$ over the range $500 - 1000^\circ\text{C}$. That is why, in case of large temperature variations, one has to specify the range of temperature under consideration.

Another point of interest has to do with the anisotropy of the expansion in case of some crystals. For example, ZnO crystals are of the closed packed hexagonal type. The value

of $\alpha = 8 \times 10^{-6} \text{ K}^{-1}$ in a direction parallel to the c-axis while it is $4 \times 10^{-6} \text{ K}^{-1}$ in a perpendicular direction. The measured value of α for the polycrystalline oxide will lie between these two values.

Finally, the volume expansion coefficient β is defined as:

$$\beta = \frac{1}{V_0} \frac{dV}{dT} \text{ K}^{-1} \quad (4.2)$$

Where V_0 is the initial volume and V the volume at temperature = T K.

If the expansion is considered to take place uniformly in all three dimensions, it is called **isotropic expansion**. This way, one can assume that expansion is similar to that of a cube of edge = L , hence $V = L^3$ and $dV \approx 3L^2.dL$

Dividing by $V_0 = L_0^3$, we get:

$$\frac{dV}{V_0} = \frac{3L^2 dL}{L_0^3}$$

Dividing by dT , we get:

$$\beta \approx 3.\alpha \quad (4.3)$$

4.2.2 Thermal conductivity

The definition of thermal conductivity is obtained from the Fourier law of thermal conduction. If heat flows at a rate Q across a wall of thickness x , such that the drop in temperature is ΔT , then:

$$Q = k.A. \frac{\Delta T}{\Delta x} \quad (4.4)$$

Here A is the cross sectional area and the units of Q are J.s^{-1} or W (Watt). The thermal conductivity k has therefore the units: $\text{W.m}^{-1}.\text{C}^{-1}$

Table (4.2) shows the thermal conductivity of some common ceramic materials together with the temperature at which it has been determined. This is because thermal conductivity is very sensitive to temperature (See for example Al_2O_3 in the table).

Table 4.2: Thermal conductivities of some common ceramic materials

Material	C	SiC	MgO	Al_2O_3	Al_2O_3	Glass	Porcelain	Concrete	Gypsum
$k \text{ W.m}^{-1}.\text{C}^{-1}$	5.1	60	37	30	6.3	0.6-2	1.5	0.8	0.4
Temp °C	600	600	200	100	1000	100	200	25	25

Thermal conductivity is also very sensitive to the presence of any secondary phase, particularly porosity. For example, while the value of k for pure MgO at 200°C is 37, it is about 0.5 for powdered magnesia. Also, the thermal conductivities of insulating materials is one to two orders of magnitude lower than low porosity materials. In Table (4.3) are shown the values of k for some ceramic insulating materials.

Table 4.3: Thermal conductivities of some ceramic insulating materials

Material	Asbestos		Ins. fire brick		Diatomite		Cellular concrete	
$k \text{ W.m}^{-1}.\text{°C}^{-1}$	0.15	0.2	0.09	0.19	0.07	0.12	0.08	0.095
Temp °C	0	200	200	800	200	900	25	120

The effect of porosity (ϵ) on the thermal conductivity of a rigid body can be predicted using more than one model. The pore size also plays a role since if pores are large enough, thermal radiation begins to play a role, besides conduction, in heat transfer across the body. For small uniformly distributed pores, the relation is linear taking the form:

$$k = k_0.(1 - \epsilon) \tag{4.5}$$

Where, k_0 is the thermal conductivity at zero porosity.

4.3 Mechanical properties

4.3.1 General considerations

When a ceramic sample is tested for tension, its stress – strain diagram usually differs considerably from that of metals or polymers. Figure (4.1) shows a comparison between the shapes of the stress – strain curves of the three materials. Metals begin to yield after a reversible elastic period and ductile failure occurs at a relatively high strain. Polymers, on the other hand, usually display a very short elastic strain, yielding very rapidly at low stress over large strain range because of the chain nature of polymers. Finally, ceramic materials show a **brittle fracture** without any appreciable yield after a reversible elastic strain. Their tensile strength is much lower than metals, although usually higher than polymers.

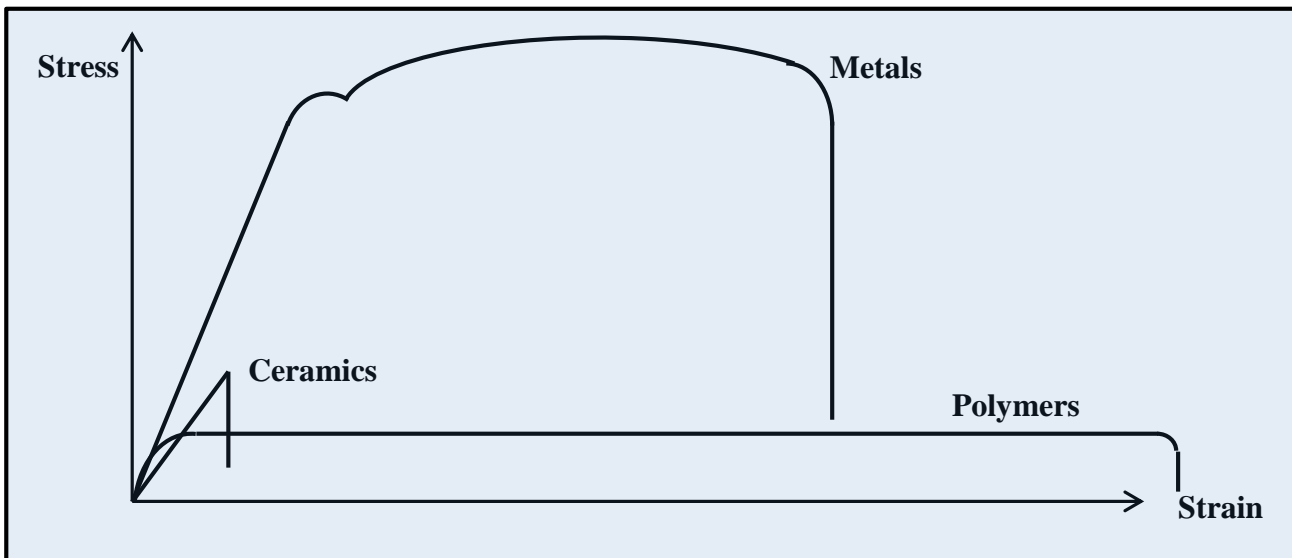


Fig (4.1) Stress – Strain diagrams for different engineering materials

The work per unit volume required to cause fracture is known as **Toughness**

$$\frac{W}{V_0} = \frac{1}{V_0} \int F \cdot dl \quad (4.6)$$

Where, V_0 is the original volume of sample.

If σ is the applied stress, then: $F = A \cdot \sigma$

And if ϵ is the strain, then: $d\epsilon = \frac{dl}{l_0}$

Hence, from equation (4.6):

$$\begin{aligned} \frac{W}{V_0} &= \frac{1}{Al_0} \int A \cdot \sigma \cdot dl \\ \frac{W}{V_0} &= \frac{1}{l_0} \int \sigma \cdot dl \end{aligned} \quad (4.7)$$

Hence, toughness is the area under the stress – strain curve. It can be seen therefore from Figure (4.1) that compared to metals and polymers, ceramic materials require the least energy for fracture. That is, they have the **lowest toughness**.

We should note that, since ceramic materials only display a linear stress – strain behaviour, then it is possible to obtain W/V_0 by simply calculating the area of the triangle:

$$\text{Area} = \frac{W}{V_0} = \frac{1}{2} \epsilon_{max} \sigma_{max}$$

If the Young's modulus of the material is Y , then:

$$Y = \frac{\sigma_{max}}{\epsilon_{max}}$$

So we get the following expression for toughness:

$$\frac{W}{V_0} = \frac{\sigma_{max}^2}{2Y} \quad (4.8)$$

The values of tensile strengths of ceramic polycrystalline materials are generally much lower than those of metals. This is due to more than one reason: If the material has an open structure, then no much energy will be required to pull away atomic planes of low atomic density from their positions. Also, because of the mechanism of brittle failure, to be discussed in the next section, the cracks propagation is very rapid, causing fracture under relatively low loads.

It is also worth noticing that the presence of pores in ceramic bodies strongly affects the strength. It was possible to correlate the strength to porosity by the relation:

$$\sigma = \sigma_0 \cdot e^{-c \cdot \epsilon} \quad (4.9)$$

This expression is valid for all types of mechanical strengths.

4.3.2 Mechanism of brittle fracture

Brittle fracture occurs suddenly, at stresses much below the theoretically calculated stress. The accompanying plastic deformation (yield) is almost inexistent. The mechanism of brittle fracture was first explained by **Griffith** and can be summarized in the following.

In brittle materials, there are small microcracks at the tip of which stress is concentrated. This tip stress is given by:

$$\sigma_{tip} = 2\sigma \sqrt{\frac{a}{r}} \quad (4.10)$$

Where, σ is the applied stress, a the length of crack and r its radius of curvature as shown in Figure (4.2).

It can be proven that the minimum stress to be applied in order for a crack to propagate can be obtained from the following equation:

$$\sigma_{min} = \sqrt{\frac{YG_c}{\pi a(1-\nu)^2}} \quad (4.11)$$

Where,

Y is the Young's modulus Pa

G_c is the work per unit area required to cause fracture J.m⁻²

ν is the Poisson ratio of the material

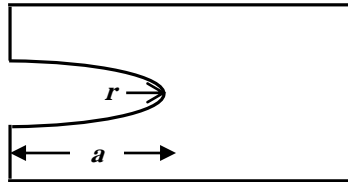


Fig (4.2) Model of a crack to which equation (4.10) applies

We note from this equation that a longer crack (large value of a) means that a lower stress is necessary for its propagation. For metals, the value of G_c is usually high. For example it is 40 J.m⁻² for steel, while being very low for ceramic materials. For alumina $G_c = 0.06$ J.m⁻² and for glass it is 0.003 J.m⁻².

G_c is representative for the material toughness. **The fracture toughness** of a brittle material is defined by:

$$K_{1C} = \sqrt{YG_c} \text{ MPa.m}^{1/2} \quad (4.12)$$

It is an inherent property of a material. So, equation (4.11) can be rewritten in the form:

$$\sigma_{min} = \frac{K_{1C}}{\sqrt{\pi a(1-\nu)^2}} \quad (4.13)$$

A more conservative value of σ_{min} can be obtained by neglecting the $(1 - \nu)^2$ term. Equation (4.13) therefore simplifies to:

$$\sigma_{min} = \frac{K_{1C}}{\sqrt{\pi a}} \quad (4.14)$$

This is the **Griffith criterion** for brittle fracture.

In Table (4.4) are listed some values of K_{1C} , Y , and ν .

The presence of large grains due to exaggerated grain growth during firing has a negative effect on the strength. This is due to several reasons. One reason is that large grains tend to be anisotropic in their expansion. This will lead to the appearance of internal stresses that may exceed the value of the minimum stress required for crack propagation (Equations 4.13 or 4.14).

Another reason has to do with the presence of surface flaws due to machining or accidental damage. These form cracks at the intersection of grain boundaries with the surface. They usually extend one grain length inside the material. If the grains are small in size, they will stop extending rapidly while in case of large grains, they may extend deeply in the bulk of the solid

Table 4.4: Fracture toughness, Young’s modulus and Poisson ratio of some ceramic materials (After Barsoum)

Material	Al ₂ O ₃	MgO	Quartz	Fused SiO ₂	ZrO ₂ cubic	Hot P SiC	Glass ceramic	Sodalime glass
K_{1C} MPa.m ^{1/2}	2 – 6	2.5	-----	0.8	3-3.6	3 – 6	2	0.82
Y GPa	390	300	94	72	200	440	100	69
ν	0.25	0.18	0.17	0.16	0.3	0.193	0.3	0.25

Example 4.1

A MgO plate is subjected to a tensile stress of 12 MPa. A crack inside this sample has a length of 0.1 mm. Its radius of curvature at its tip is 0.02 mm. Calculate the actual stress developed at the tip of the crack.

Solution:

$\sigma = 12$ MPa

$a = 0.1$ mm

$r = 0.02$ mm

From equation (4.10):

$\sigma_{tip} = 2 \times 12 \times \sqrt{5} = \mathbf{53.66}$ MPa

This is an increase of about 450% of the applied stress.

Example 4.2

A MgO plate is subjected to a tensile load of 5 kN. The surface under tension is 15×15 mm in dimensions. Under this load, what is the minimum size of crack that would propagate across the plate?

Solution:

$$\sigma = 5000 / (15 \times 15) = 22.2 \text{ MPa}$$

From Table (4.4):

$K_{1C} = 2.5$ and $\nu = 0.18$, hence from equation (4.13):

$$22.2 = \frac{2.5}{\sqrt{3.1416 \times a \times (1 - 0.18)^2}}$$

From which,

$$a = \mathbf{6 \text{ mm}}$$

If we use the Griffith equation (4.14), we get:

$a = \mathbf{4 \text{ mm}}$, which is a more conservative figure.

Example 4.3

A plate of alumina contains a sharp notch of 0.1 mm in length. What is the maximum tensile load that can be applied without causing fracture?

Solution:

We apply the Griffith condition (equation 4.14):

From Table (4.4), for Alumina, $K_{1C} = 2$ (minimum value), hence:

$$\sigma_{min} = \frac{2}{\sqrt{\pi \times 0.0001}} = \mathbf{112.8 \text{ MPa}}$$

4.3.3 Compressive loading

As we have seen, the tensile brittle failure is due to crack propagation when the stress exceeds a certain critical value. In case of compressive loading, the cracks tend to form parallel to the direction of loading and their propagation is less harmful than in case of tension (Figure 4.3). The minimum stress required to cause failure can be calculated from:

$$\sigma_{min} = \frac{15K_{1C}}{\sqrt{\pi a_{av}}} \tag{4.15}$$

Where, a_{av} is the average crack size, rather than an individual size in case of tension.

We can see from the above equation that the compressive stress required for failure in case of compressive loading is about 15 times higher than in case of tension.

4.3.4 Toughening of ceramics

As previously explained, ceramic materials suffer from low toughness. In the last two decades, efforts were deployed to increase their toughness.

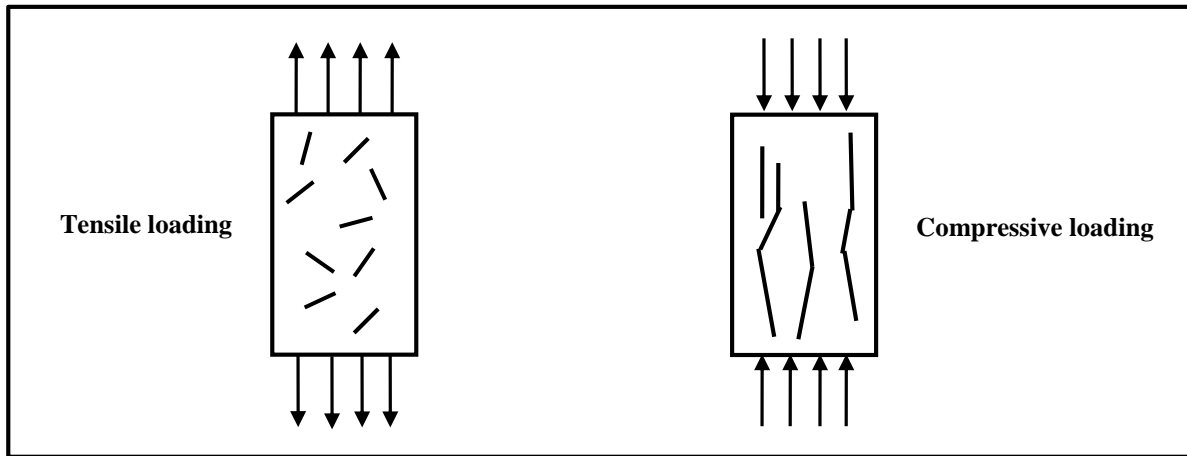


Fig (4.3) Crack propagation in tension and in compression

One of the most common methods is to add zirconia (ZrO_2). It has been discovered that the addition of zirconia has for effect to increase both the fracture stress and the fracture toughness of ceramics. This is due to the allotropic transition of zirconia on cooling at about $1170^\circ C$, from the high temperature tetragonal to the low temperature monoclinic phase. This is accompanied by about 4% increase in volume and develops a large amount of strain in the solid. Now, consider a ceramic material to which is added this oxide. If it is heated above the transition temperature, the tetragonal phase will be formed.

If now the solid is rapidly cooled, then the tetragonal phase will be preserved in a metastable state. The transition to the low temperature monoclinic phase can be triggered, however, by approaching cracks. These can supply enough energy to cause this transition. As soon as this transition takes place, the developed compressive strains are enough to stop crack propagation. A lot more energy is now required for this propagation to go on, hence, the increase in toughness.

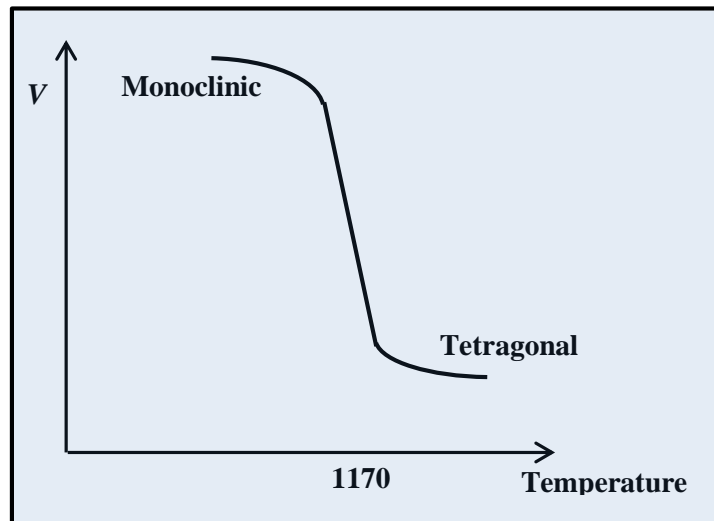


Fig (4.4) Volume change of zirconia on allotropic transition

4.3.5 Thermal stresses

(a) Thermal stresses in isotropic solids

Polycrystalline materials made of one single phase expand on heating equally in all directions. In order that thermal stresses develop, they have to be restricted from movement. A classical example is the refractory bricks used to line the interior of firing kilns. As temperature is raised, expansion takes place and compressive stresses develop within the bricks. If their magnitude exceeds the allowable limit, then cracks will develop to relieve these stresses and failure will follow.

The calculation of such stresses is based on the definition of the linear coefficient of expansion α . The linear expansion usually varies linearly with temperature, so that equation (4.1) can be written in the form:

$$\alpha = \frac{1}{L_0} \frac{\Delta L}{\Delta T} = \frac{\epsilon}{\Delta T}$$

Where, ϵ is the strain.

Since $\sigma = Y.\epsilon$, then we get the following expression for the thermal stress σ_{th} :

$$\sigma_{th} = Y.\alpha.\Delta T \quad (4.16)$$

Example 4.4

An alumina brick is horizontally confined between two vertical surfaces. What is the maximum temperature to which it can be heated before failure occurs if the maximum allowable stress is 120 MPa? ($Y = 30 \text{ GPa}$)

Solution:

The value of α for alumina is $8 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$ (Table 4.1) and $Y = 30 \times 10^9 \text{ Pa}$. Hence, from equation (4.16):

$$120 \times 10^6 = 8 \times 10^{-6} \times 30 \times 10^9 \Delta T, \text{ from which: } \Delta T = 500^\circ\text{C}$$

We note that the value of Y given in this example is much lower than that given for alumina in Table (4.4). This is since this latter figure is for pure alumina while an alumina brick contains some porosity which strongly affects the value of Y .

We also notice that the value of ΔT is relatively low since alumina bricks are usually used when temperatures exceed 1400°C . That is why dilatation should be taken into consideration in designing the walls of a furnace by installing expansion joints or having empty spaces between the adjoining surfaces that will eventually close during the firing run.

(b) Thermal stresses in anisotropic solids

In case of bodies containing more than one phase, the problem is complicated by the fact that each phase has its own coefficient of expansion. Therefore, stresses arise because of the difference in expansion or contraction of the different phases upon changes in temperature.

If α_1 and α_2 represent the linear expansion coefficients of the two phases in a two phase body, with $\alpha_1 > \alpha_2$, then the thermal stress developed can be calculated by the equation:

$$\alpha = \frac{(\alpha_1 - \alpha_2)\Delta T}{\frac{1}{Y_1} + \frac{1}{Y_2}} \quad (4.17)$$

Here, Y_1 and Y_2 are the Young's moduli of the two phases.

The stresses arising from heating are compressive. If the difference term $\alpha_1 - \alpha_2$ is small, then no stresses will arise since the two phases will be expanding practically at the same rate.

(c) Thermal shock

Whenever a ceramic body is heated, then rapidly cooled down, the external surface will cool much more rapidly than the bulk of the solid. This temperature gradient may be severe enough to generate stresses exceeding the allowable limit. This situation is common in refractory bricks placed into batch kilns that are subjected to repeated cycles of heating and cooling. This causes surface cracks first to appear that are followed by rapid propagation. This phenomenon is known as **thermal spalling**.

The ability of a ceramic body to resist spalling is related to its mechanical characteristics. A solid having a good thermal shock resistance should have a low coefficient of expansion, a low Young's modulus, a high tensile strength and a high thermal conductivity to reduce the thermal gradient set in. A criterion given by **Kingery** was later modified by **Barsom** to define the thermal shock resistance as:

$$R_{ths} = \frac{k\sigma(1-2\nu)}{\alpha Y} \text{ W.m}^{-1} \quad (4.18)$$

Where, k is the thermal conductivity $\text{W.m}^{-1}.\text{C}^{-1}$

Typical ceramic solids of high thermal shock resistance are SiC ($R_{ths} = 17300 \text{ W.m}^{-1}$) and hot pressed Si_3N_4 ($R_{ths} = 16800 \text{ W.m}^{-1}$), besides glass ceramics which have a very low expansion coefficient. For comparison, for hot pressed alumina, $R_{ths} = 640 \text{ W.m}^{-1}$.

4.3.6 Measurement of mechanical properties

(a) Tensile strength

The tensile strength of ceramic materials is determined experimentally by preparing elongated specimens having a central neck. The specimen is then loaded at a strain rate $\sim 10^{-6}$ mm/mm. The tensile strength is then calculated by dividing the fracture load by the cross sectional area of the neck at which fracture occurs.

(b) Compressive strength

In that case, the specimen is usually cylindrical with a length to diameter ratio of 1:1 – 2:1 although sometimes cubic samples are used. The compressive strength is also calculated by dividing the fracture load by the loaded area.

(c) Bending strength (Modulus of Rupture)

This property is of importance in case of thin products such as tiles. The most common practice is to use the **three point bending test**. In this test, the specimen is placed on two supports and a central load is applied using a sharp blade having the same breadth as the

specimen. If the fracture load is W , the distance between the supports L , the breadth of sample b and its thickness d , then the modulus of rupture is calculated using the formula:

$$\text{MOR} = \frac{3WL}{2bd^2} \quad (4.19)$$

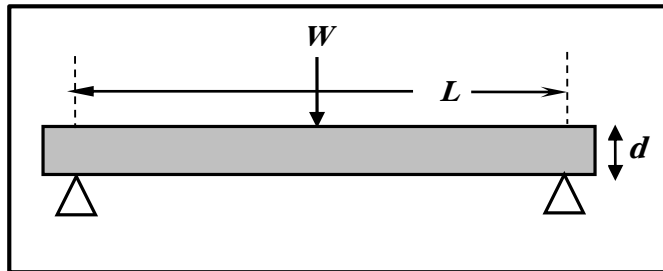


Fig (4.5) Three point bending test for the measurement of the MOR

In this test, the lower surface of the tested specimen is under tension while the upper part is under compression. (Figure 4.5)

(d) Hardness

This is the property that measures the ability of a material to resist scratching. It can be measured in several ways. An empirical method consists of comparing the scratching behaviour of the material to a set of 10 standard materials, starting from 0 for talc to 10 for diamond, a scale known as the Moh’s scale of hardness. (Figure 4.6)

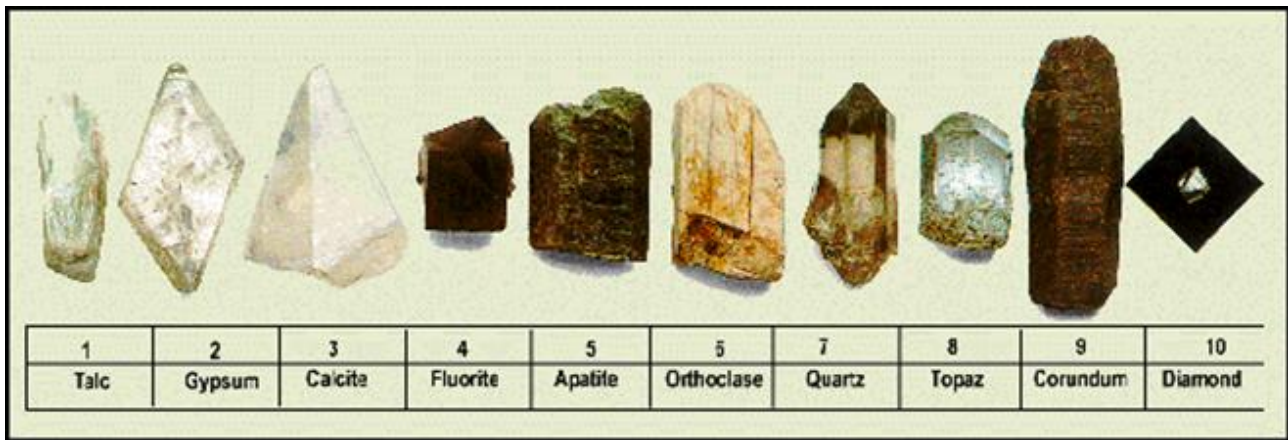


Fig (4.6) Moh’s scale of hardness

A more reliable method is to determine the **Vickers hardness number (VHN)**. In this method a diamond having the shape of an inverted pyramid is applied under a definite pressure onto the surface of the material. The indentation produced has usually the form of a crater (Figure 4.7). Modern equipment is calibrated to directly measure the hardness out of

the dimensions of the crater produced. This figure represents a stress term and is usually expressed in GPa. Table (4.5) shows some typical values.

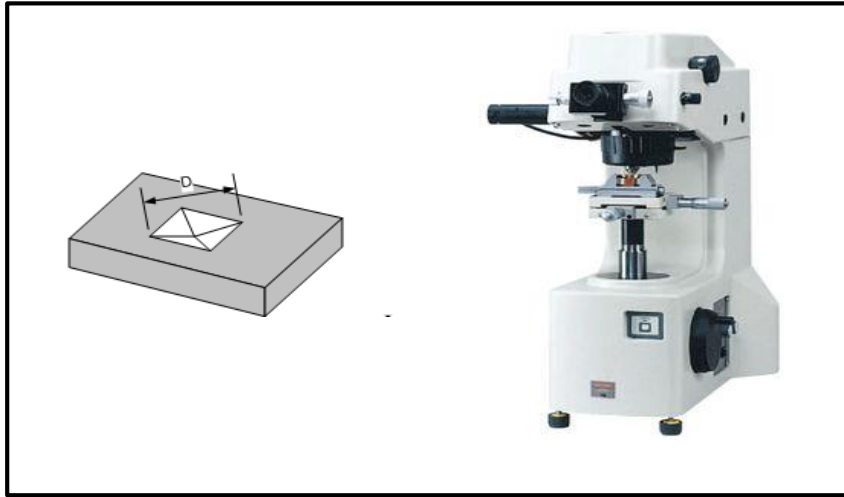


Fig (4.7) Vickers hardness testing

Table 4.5: Typical VHN values for some ceramic materials

Material	Al ₂ O ₃	MgO	SiO ₂	TiO ₂	SiC	ZrO ₂	Glass
VHN GPa	20	8	12	10	30	14	5.5

(e) Impact strength

This test is sometimes required in case of large brittle products, such as gypsum panels. It may be performed in several ways. One way is to apply an impact on the surface of the panel by using a pendular rod of standard weight. This impact is repeated until cracks appear on the surface of the panel. The total energy required to produce these cracks is a measure of the impact strength in KJ. (Figure 4.8)

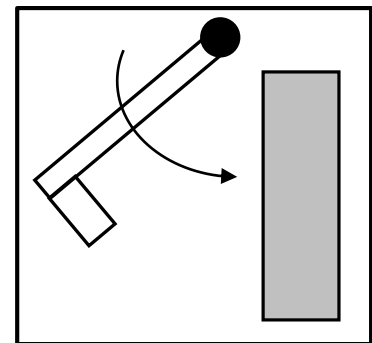


Fig (4.8) Impact test

In a simpler method, a steel ball of definite size and mass m is allowed to drop over the surface of the panel from a height h . If after n falls, cracks appear on the surface then the total work is:

$$W = n.m.g.h \text{ J.} \tag{4.20}$$

It is to be noted however, that this method is not standardized and has to be used only for approximate or comparative determination.

4.4 Electrical properties

4.4.1 Electric conductivity in solids

Consider a single atom: the electrons in its outermost energy level are those which contribute to chemical reactions and are known as valence electrons. On a macromolecular level, a solid is constituted of a set of atomic planes where atoms are in adjacent positions. Consider one such plane: The combination of valence electrons with close energy levels forms an energy band known as the **valence band** (Fig. 4.9)

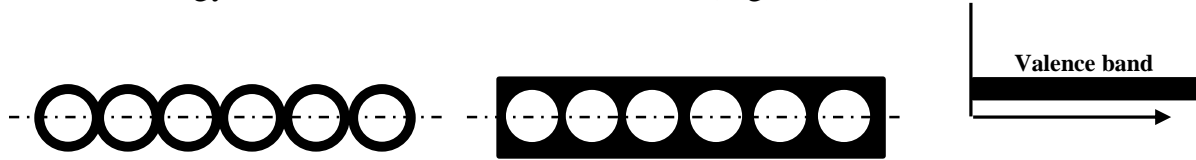


Fig (4.9) The valence band

If enough energy is transferred to the material, then some valence electrons can undergo leaps from their energy state to higher energy levels in which they are no more bounded by nuclear attraction. These are then called **free electrons** and their energy levels lie in the **conduction band**. There is a forbidden **energy gap** between the valence and the conduction bands. The width of that gap leads to classifying solid materials into three categories (Fig. 4.10):

- If the band gap width is large (Few eV) then the valence electrons cannot easily reach the conduction gap when the material is energized. This class of solids is known as **insulators**. Most ceramic materials are of that type (like alumina, calcium oxide, etc.)
- If the band gap width ranges about 1 eV then, although most of the electrons still lie in the valence gap, a minor fraction can “jump” to the conduction band. Such materials are termed **semiconductors** like silicon, germanium and some ceramic materials like BaTiO₃.
- If the energy levels of the two gaps are comparable, then the gap vanishes and all valence electrons are available for conduction, behaving as free electrons. This is the case of **conductors** like silver, copper, etc.

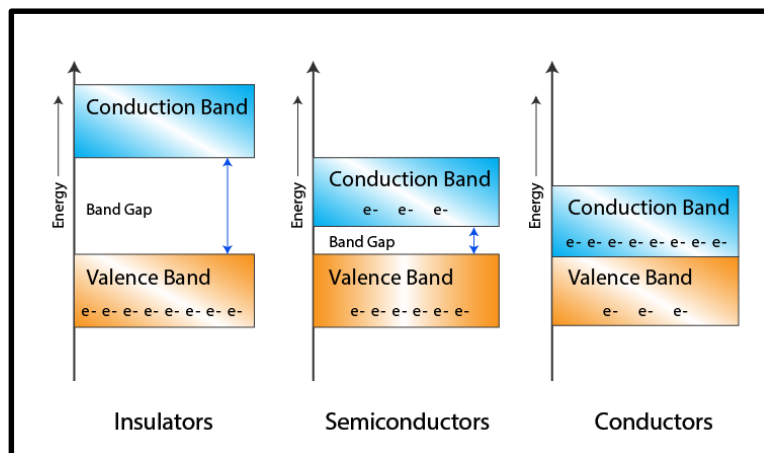


Fig (4.10) Energy bands

4.4.2 Dielectric ceramics

In order to understand the use of some ceramic materials as dielectrics, it should be remembered that most ceramic crystals display to different extents charge polarization upon the application of an external electric field.

Consider two parallel plates separated by a distance d in vacuum. If these plates are connected to an external DC source, then there will pass a current in the circuit that will decay very rapidly to a zero value. The amount of stored charge is hence very low and can be measured by the vacuum capacitance defined by:

$$C = \frac{\epsilon_0 \cdot A}{d} \tag{4.21}$$

Where, ϵ_0 is a constant known as the **space permittivity** = $8.85 \times 10^{-12} \text{ C}^2 \cdot \text{J}^{-1} \cdot \text{m}^{-1}$

A is the area of each plate and C , the vacuum capacitance in Farad ($\text{C} \cdot \text{V}^{-1}$)

If now, a dielectric material is introduced between the two plates, then, due to the polarization of charges, the current produced will remain a longer time before decaying (Fig. 4.11). Since the area under the $I - t$ curve represents the total charged stored, then this will mean that the introduction of the dielectric material has had for effect to increase the storage capacity. The capacitance can then be calculated from an equation similar to (4.21):

$$C = \frac{\epsilon \cdot A}{d} \tag{4.22}$$

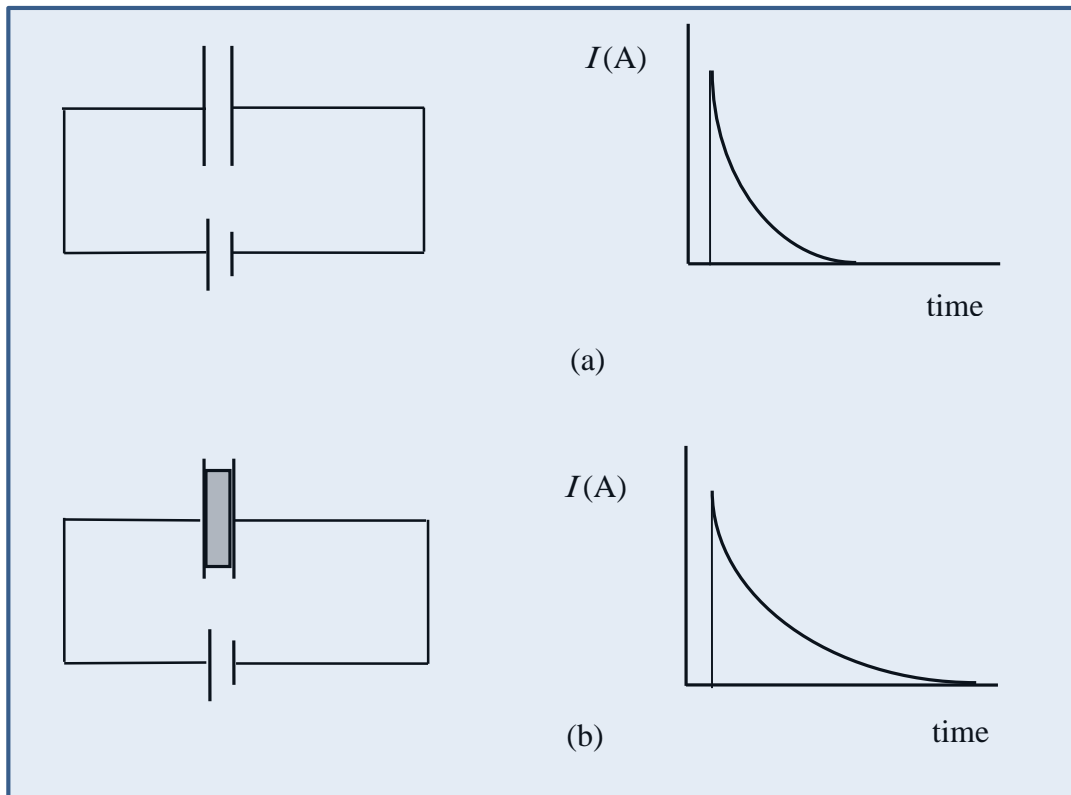


Fig (4.11) Effect of introducing a dielectric material on the amount of charge stored

ϵ is known as the **dielectric constant** of the material.

The ratio between the dielectric constant and the space permittivity is known as the **relative dielectric constant K'** .

$$K' = \frac{\epsilon}{\epsilon_0} \quad (4.23)$$

Ceramic materials fall generally into two categories: Most of these materials have values of K' in the range 5 – 15, while some materials having the perovskite structure (like BaTiO₃) may have extremely high values in the range $10^2 \sim 10^3$.

An ideal dielectric material would store all the incoming charge and deliver it, upon discharge without any loss. Actually, however, there is some energy dissipation that is proportional to the applied frequency, the applied field and a material characteristic known as the **dielectric loss K''** . A highly conducting material will dissipate all the incoming charge and hence has a high dielectric loss. So, since ceramics are good electrical insulators, they are commonly used as capacitors.

4.4.2 Electrical conductivity in ionic ceramics

Although ceramics are bad electrical conductors, ionic species can show some solid state current conductance at temperatures near their melting points. This is the case of NaCl for example. The conductivity is the reciprocal of the electrical resistivity ρ . It is defined by

$$A = \frac{R.L}{A} \quad (4.24)$$

Where, A is expressed in $\Omega^{-1} \cdot m^{-1}$

R is the resistance in Ω (Ohm),

A is the cross sectional area of the conductor (m^2) and L its length (m).

If an ionic solid is placed in an electric field, the electric conductivity is not due, as in metals, to the motion of free electrons (since there aren't any) but, rather, to the motion of ionic charges. Since the ionic radius of cations is much smaller than that of anions, the diffusion of the former will be mainly responsible for the charge transfer, and hence the flow of current. This diffusion is a thermally activated process and therefore takes place when the solid is being heated. This diffusion, as measured by the conductivity, follows an Arrhenius type equation in the form:

$$A = A_0 \cdot e^{-\frac{E}{RT}} \quad (4.25)$$

Where: A_0 is a constant and E is an activation energy term ($J \cdot mol^{-1}$)

The value of E is the sum of two terms: The first is half the energy required to release a Schottky cation – anion pair ($\Delta H_s/2$), and the second, the energy required to cause the migration of the cation through the lattice (ΔH^+). The above equation can be linearized into the form:

$$\ln A = \ln A_0 - \frac{E}{RT} \quad (4.26)$$

And the slope should be equal to $\frac{-\frac{\Delta H_S}{2} - \Delta H^+}{R}$

Actually, a plot of $\ln A$ vs $1/T$ produces two straight lines instead of one line. (Figure 4.12). The reason for that behavior is that, at high temperatures both mechanisms take place and charge is transferred due to cation motion across the lattice. The slope of this line is then as indicated above.

At low temperatures, there is not enough energy for a Schottky pair to form and conductivity is only due to the motion of impurity ions. That is why the high temperature line corresponds to **intrinsic diffusion** while the low temperature portion corresponds to **extrinsic diffusion**. The slope of this portion reduces to $\frac{-\Delta H^+}{R}$

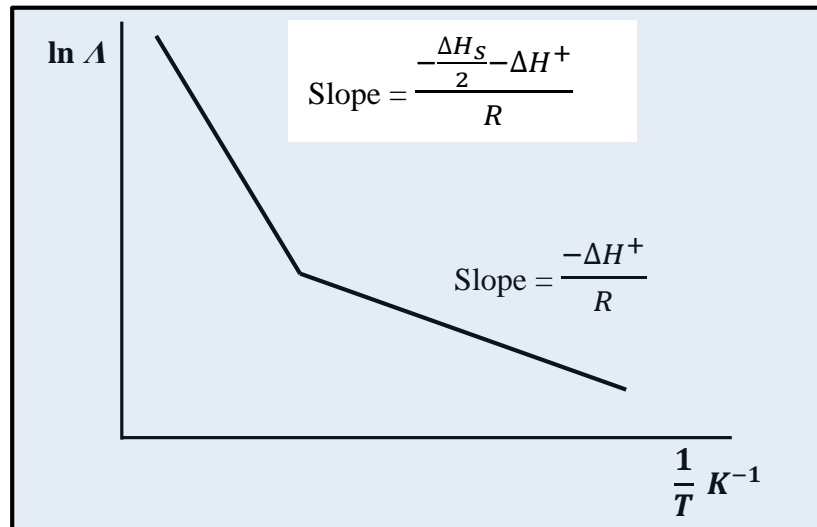


Fig (4.10) Ionic conductivity

4.5 Magnetic properties

4.5.1 Origin of magnetism

When electric charges are in motion in vacuum, a magnetic field is generated. If the intensity of this field is H , then the **magnetic flux density B** is defined as:

$$B = \mu_0.H \quad (4.27)$$

Where, H is expressed in $A.m^{-1}$

B is expressed in $Wb.m^{-2}$ (Tesla)

μ_0 is called the vacuum permeability = $4\pi.10^{-7} Wb.A^{-1}.m^{-1}$

If the motion of charges is not in vacuum, but within a solid, then equation (4.27) can be rewritten as:

$$B = \mu_0.(H + M) \quad (4.28)$$

Where, M is known as the **magnetization**.

The product of the magnetization by the volume is called the **magnetic moment**:

$$\mu = M.V \text{ A.m}^2 \quad (4.29)$$

Now, in an atom, an electron moving around the nucleus will generate a magnetic flux consisting of two components:

First: A magnetic component due to this very motion of a charged particle. It is measured by **the orbital magnetic moment** vector μ_{orb} calculated from:

$$\vec{\mu}_{orb} = 9.27 \times 10^{-27} \sqrt{l(l+1)} \vec{n} \quad (4.30)$$

Where, l is the orbital quantum number and \vec{n} a unit vector normal to the plane of the sub orbit.

Second: A magnetic component due to the electron spin calculated from the **spin magnetic moment** vector μ_{spin} calculated from:

$$\vec{\mu}_{spin} = 1.85 \times 10^{-26} \sqrt{s(s+1)} \vec{n} \quad (4.31)$$

This effect appears only if the atom possesses unpaired electrons.

Since an atom possesses, in general, many electrons, then the total orbital moment vector is obtained by the vector sum of all $\vec{\mu}_{orb}$'s obtained from equation (4.30) and the total spin magnetic vector is obtained by summing up all $\vec{\mu}_{spin}$'s obtained from equation (4.31).

The net resultant of all magnetic vectors is the vector

$$\vec{\mu}_{tot.} = \sum \vec{\mu}_{orb} + \vec{\mu}_{spin} \quad (4.32)$$

When no external field is applied, magnetic moment vectors take random directions. It is only when an external field is applied that they start arranging in the direction of the field or in an opposite direction.

4.5.2 Magnetic behavior of ceramic materials

In absence of any external field, the magnetic moment vectors of electrons are randomly oriented. When an external magnetic field of intensity H is applied, the magnetic vectors begin to align themselves in the direction of the field (Figure 4.13). According to their behavior in presence of a field, ceramic materials are divided into the following groups:

(a) Paramagnetic ceramics

These materials are attracted by the applied field and the magnetization is proportional to the intensity of the applied field. Once the field is removed the magnetic moment vectors regain their random orientations and the magnetization drops to zero. In general, ceramic materials are not paramagnetic at room temperatures.

(b) Diamagnetic ceramics

In this case, the materials also lose their magnetization as soon as the field is removed. They differ from paramagnetic materials, however, by the fact that they are repelled rather than attracted by the field. These materials display negative magnetization. Most ceramic materials fall in this category.

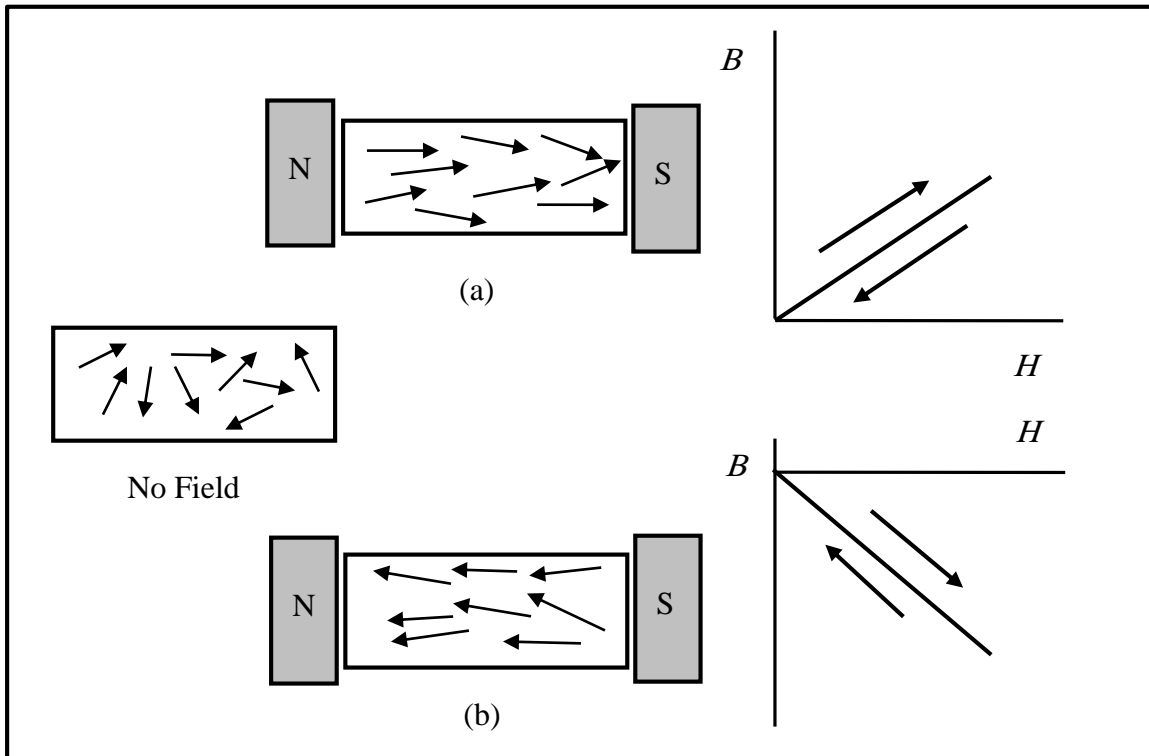


Fig (4.13) Paramagnetic and diamagnetic ceramic materials

Some ceramic materials exhibit exaggerated diamagnetism if cooled down a certain temperature. In that case, they can repel metallic materials (Meissner effect). Under these conditions, they also exhibit superconductivity, their electrical resistance approaching zero. One of the most powerful such materials is $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ (Known as 1.2.3 Y oxide). It displays an enormous magnetization that can reach 40 Tesla.

Figure (4.14) reveals the drop in resistivity (ρ) as the temperature is decreased below some critical value (T_c).

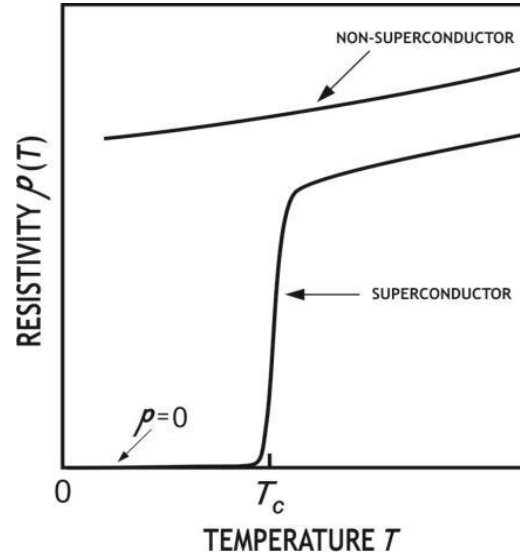


Fig (4.14) Superconductive phenomenon

On the other hand, Figure (4.15) shows the levitation of a metallic alloy over a superconductive 1.2.3Y sintered pellet.

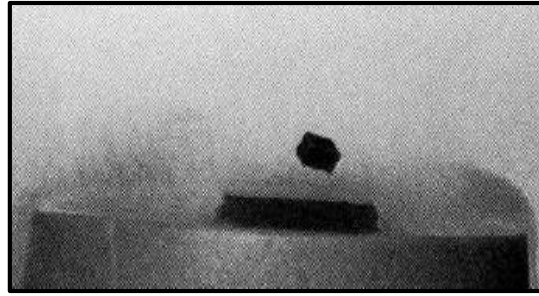


Fig (4.15) Levitation of a metallic alloy over 1.2.3Y oxide

(c) Ferrimagnetic ceramics

When such materials are subjected to an external magnetic field H , the magnetic moment vectors of neighboring atoms align in opposite directions. In theory, this should have resulted in having them cancelling each other. However, there are slight differences in their values that result in a net magnetic moment. The magnitude of that moment increases as the intensity of magnetic field is raised. This results in a saturating value of B known as **Saturation magnetization** (B_s). As the field strength is decreased, the $B - H$ curve does not reverse itself but rather, we are left with a **Remnant magnetization** (B_r) (or residual magnetization) at zero field intensity (Figure 4.16a).

In order to demagnetize the material, a certain value of negative field strength is required known as the **Coercive force**. A further increase of the magnetic field strength in the negative direction produces a saturation behavior similar to that initially observed. An increase in the value of H in the positive direction will close the **hysteresis loop**. This behavior is typical of hard ferrites discussed in Chapter 1.

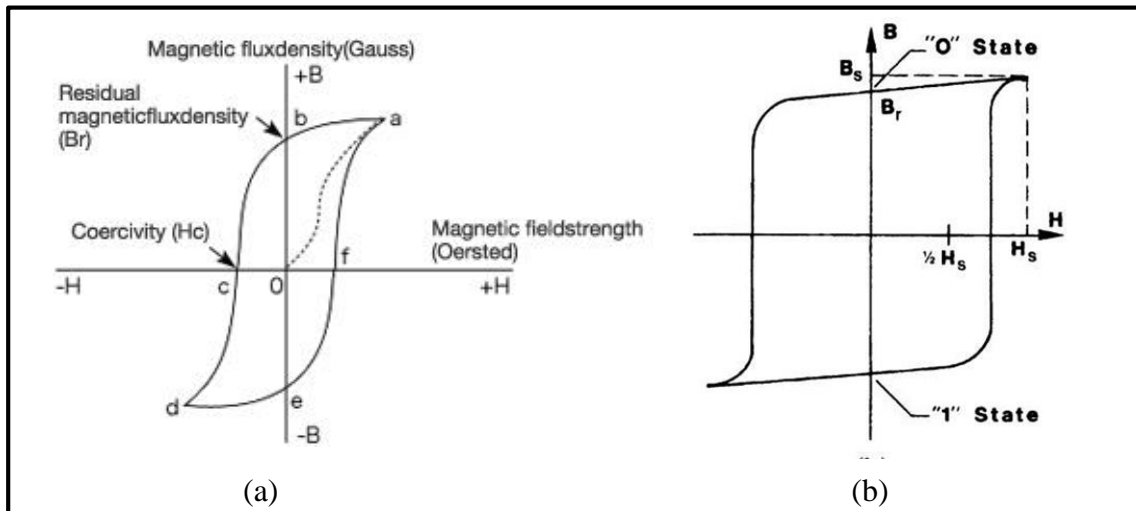


Fig (4.16) Hysteresis loop of ferrimagnetic ferrites
(a) Common loop (b) Hexaferrite

Hard ferrimagnetic hexaferrites have saturation magnetization values very close to those of remnant magnetization. This way, their hysteresis loops are often of square shape. (Figure 4.16b). These are usually used as permanent magnets.

As for **soft ferrites**, they are often characterized by a narrow hysteresis loop. They can be easily demagnetized as evidenced by the low coercive force required to get zero susceptibility (Fig.4.17). They are used to store data in computer circuits as they can easily release them as they get demagnetized.

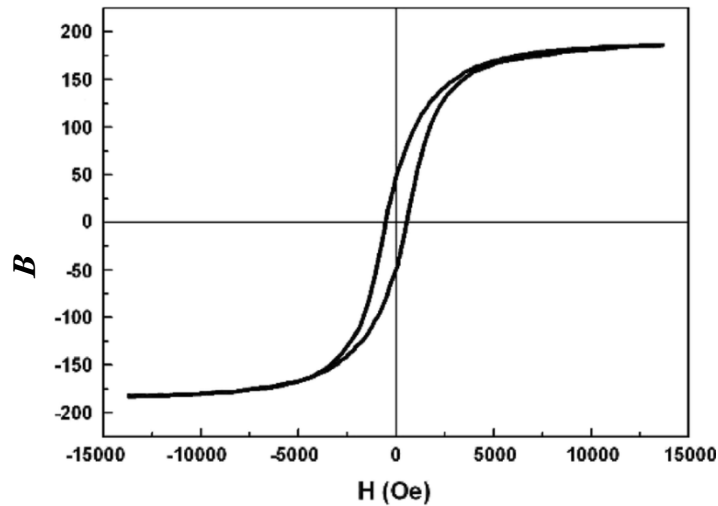


Fig (4.17) Hysteresis loop of a soft ferrite

The magnetic susceptibility of ferroimagnetic ceramics is strongly influenced by temperature since a rise in temperature will cause the disorientation of the magnetic moment vectors. The relation between B (Tesla) and T (K) follows the **Curie law**:

$$B = \frac{C}{T - T_C} \tag{4.32}$$

Where, T_C is known as the Curie temperature.

Above T_C the material behaves paramagnetically, its magnetization decreasing with increasing temperature. Below T_C , spontaneous magnetization sets in, and the material behaves as a magnet in absence of an external field. Most ceramic materials have Curie temperature in the range 600 – 900K.

(d) Ferromagnetic materials

In ferromagnetic materials, magnetic moment vectors of the electrons tend to align themselves gradually in the direction of the applied field and the material acquires rapidly the state of saturation since as the value of H is increased, the alignment becomes more pronounced and ultimately all magnetic moment vectors are aligned. Metals like iron and cobalt fall into that category and are characterized by Curie temperatures in the range 600–1400K. Some complex ceramic composites based on $PbO.ZrO_2.TiO_2$ (PZT) belong to that category.

(e) Antiferromagnetic materials

In ferrimagnetic materials each two neighboring magnetic moment vectors align in opposite directions. Since their magnitudes are not equal a net moment results. In antiferromagnetic materials, the neighboring opposite direction vectors are of equal magnitudes, therefore cancelling each other. This results in a material with no magnetic properties. Hematite (Fe_2O_3) and MnO are typical examples. Above a certain temperature (called the Neil temperature), they invert to paramagnetic behavior.

Figure (4.18) depicts the differences in behavior between the different magnetic materials.

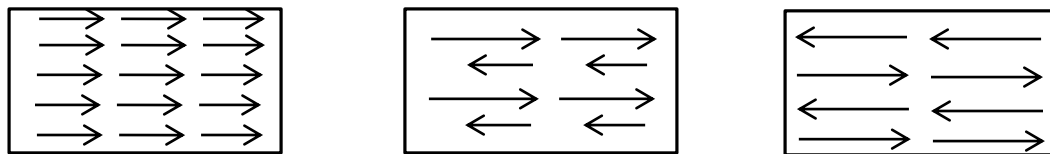


Fig (4.18) Ferromagnetic

Ferrimagnetic

Antiferromagnetic

Suggested additional reading

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