Department of Ceramic Engineering and Building Materials
3rd class
Characteristics of Ceramic Materials

Electrical properties

References :

1. Electroceramics, Second Edition: Materials _ Properties _ Applications (A. J. Moulson and J. M. Herbert)
2. Fundamentals of ceramics 2003
3. Ceramic Materials; Processes, Properties and Applications 2007

Introduction

- Engineering materials are important in everyday life because of their versatile structural properties.
- Other than these properties, they do play an important role because of their physical properties.
- Prime physical properties of materials include: electrical properties; thermal properties; magnetic properties; and optical properties.
- The electrical behaviors of engineering materials are diverse, and so are their uses in electrical applications.

Electrical conduction

- Materials are classified based on their electrical properties as conductors, semiconductors and insulators. New to this group is super conductors.
- Electrical conductivity of a material is defined in terms of ease of charge flow through it.
- Charge that flows comprised of either electrons, ions, charged holes, and their combinations.
- Ohm's law relates the current and applied voltage:

$$V = IR$$

where

V – applied voltage (volts)
I – current (amperes)
R – resistance (ohms)

Electrical conduction (contd…)

- Material’s electric resistance is NOT an intrinsic-property i.e. it depends on object geometry.
- Electrical resistivity, defined as follows, is an intrinsic property, inverse of which called conductivity.

$$\rho = \frac{RA}{l}$$

$$\sigma = \frac{1}{\rho} = \frac{l}{RA}$$

A – cross sectional area

l – length of the object

- Either conductivity / resistivity can be used to classify materials.

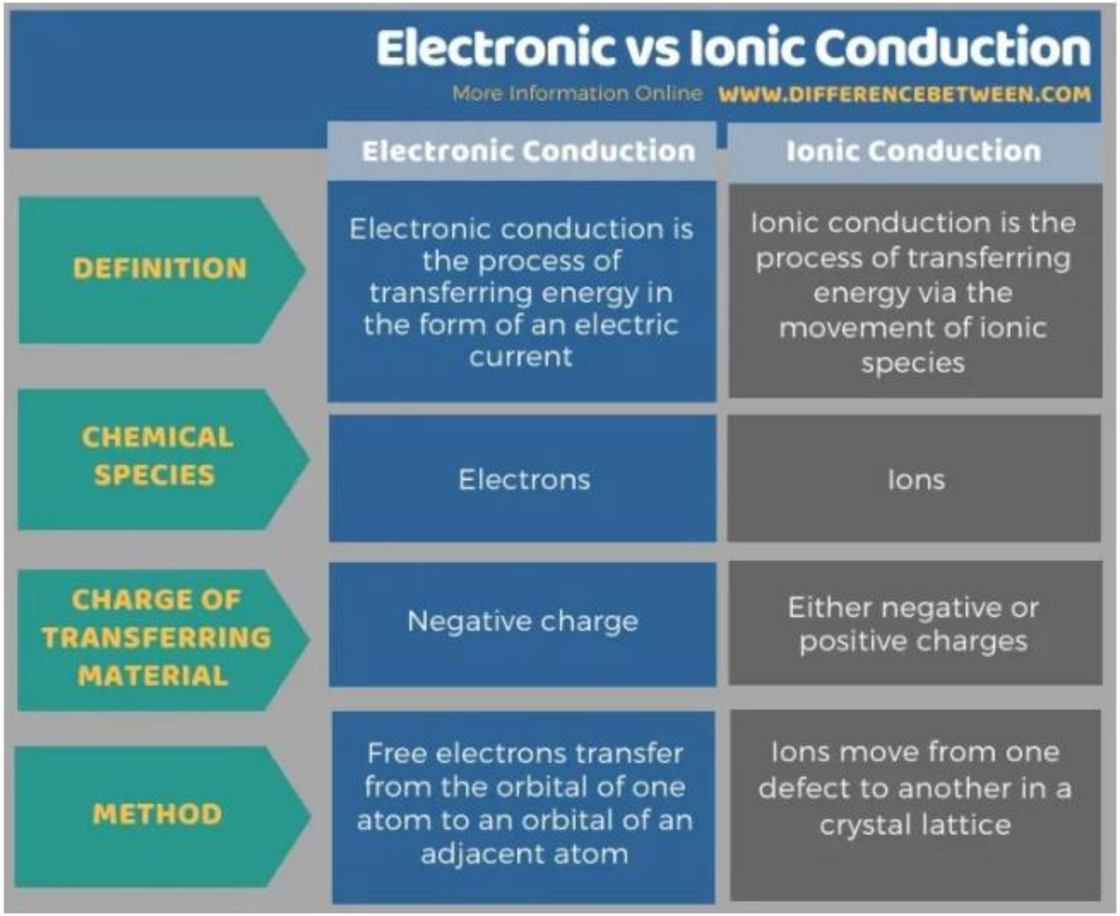
Classification – Electrical conductivity

- Conductivity of solid engineering material is observed to vary over 27 orders of power.
- Based on their conductivity, materials are classified as: conductors, semiconductors, and insulators.

Conductors	$> 10^7\ (\Omega\text{-m})^{-1}$
Semiconductors	$10^{-6} - 10^4\ (\Omega\text{-m})^{-1}$
Insulators	$< 10^{-10}(\Omega\text{-m})^{-1}$

What is the Difference Between Electronic and Ionic Conduction?

Electronic conduction and ionic conduction are two forms of energy transferring methods which are categorized based on the medium of conduction. The key difference between electronic and ionic conduction is that electronic conduction is the movement of electrons from one place to another, whereas ionic conduction is the movement of ions from one place to another.Below is a summary table of the difference between electronic and ionic conduction.



Electronic vs Ionic Conduction

More Information Online WWW.DIFFERENCEBETWEEN.COM

	Electronic Conduction	Ionic Conduction
DEFINITION	Electronic conduction is the process of transferring energy in the form of an electric current	Ionic conduction is the process of transferring energy via the movement of ionic species
CHEMICAL SPECIES	Electrons	Ions
CHARGE OF TRANSFERRING MATERIAL	Negative charge	Either negative or positive charges
METHOD	Free electrons transfer from the orbital of one atom to an orbital of an adjacent atom	Ions move from one defect to another in a crystal lattice

CERAMICS AS ELECTRICAL CONDUCTORS

1. Ceramics are usually thought of as electrical Insulators and indeed a great many of them are good electrical insulators are needed to isolate current-carrying wires.
2. many ceramics are actually very good electrical conductors and some are even superconductor Ceramics show the broadest range of electrical properties of any of the classes of material.
3. The values of electrical conductivity for ceramics vary over an enormous range—over 24 orders magnitude!
4. The conduction mechanisms in ceramics can be quite complex and may involve the movement of electrons holes, and ions; in some cases they may be "mixed," with more than one type of charge carrier responsible for current flow.
5. In the case of ceramic superconductors the current is carried by electron pairs (Cooper pairs)

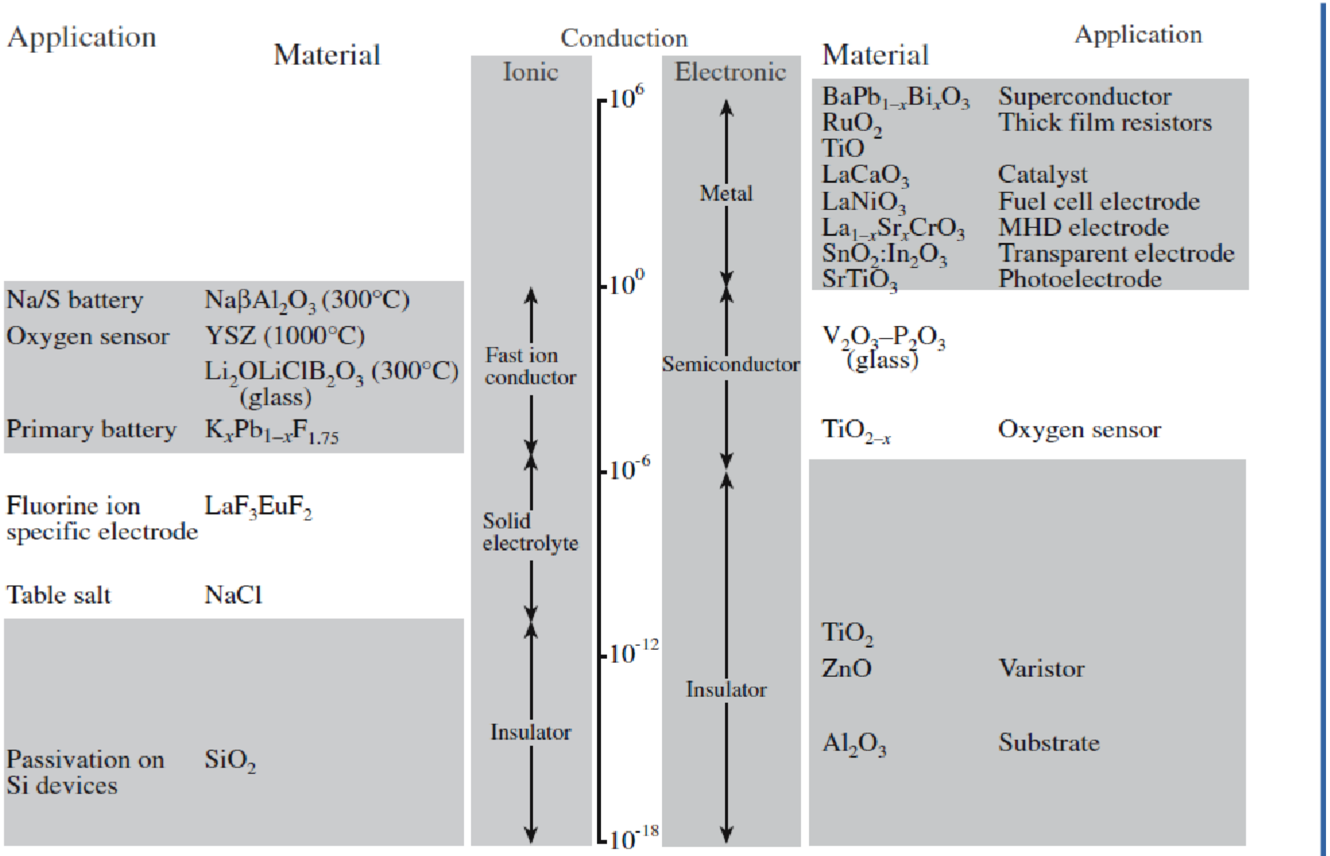


FIGURE 30.1 Range of conductivities of ceramics.

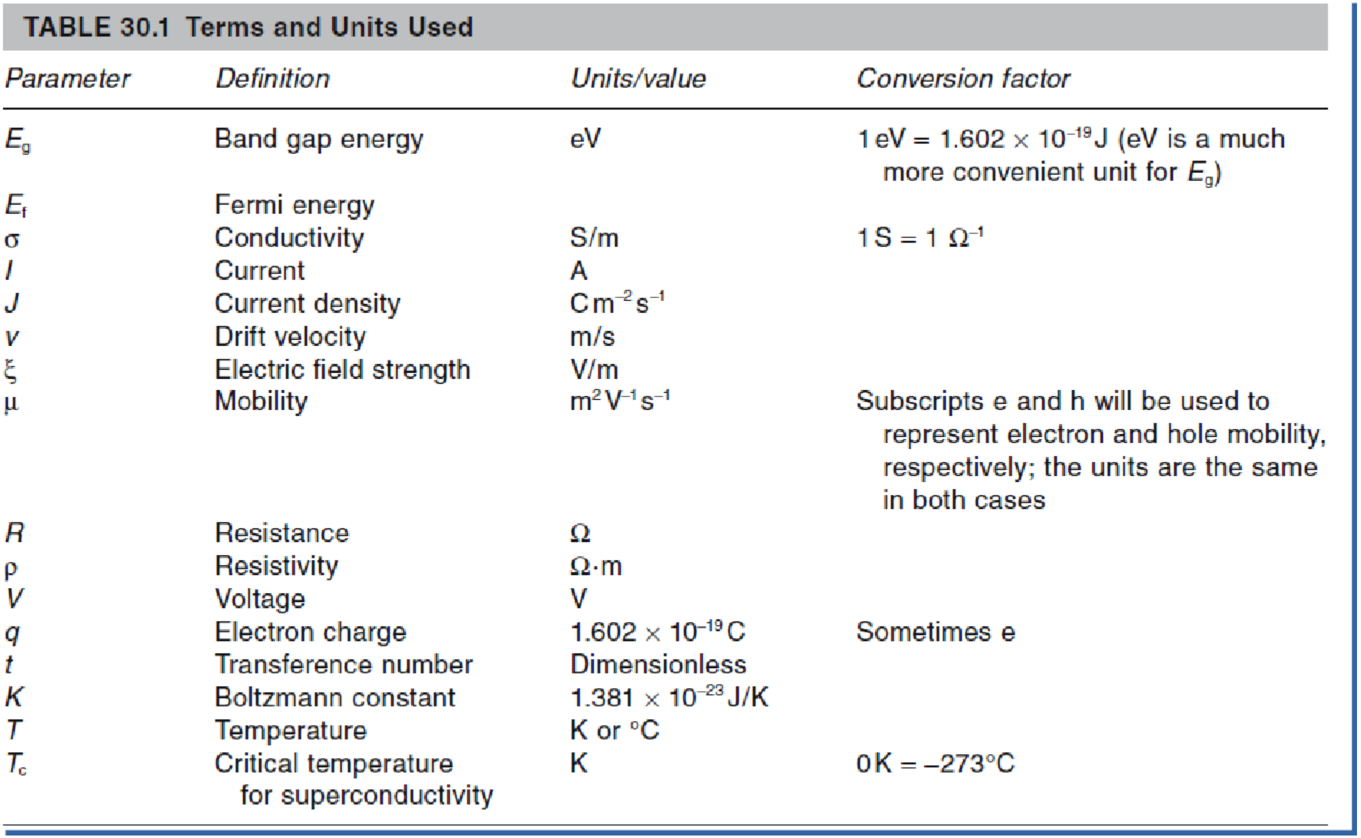


TABLE 30.1 Terms and Units Used

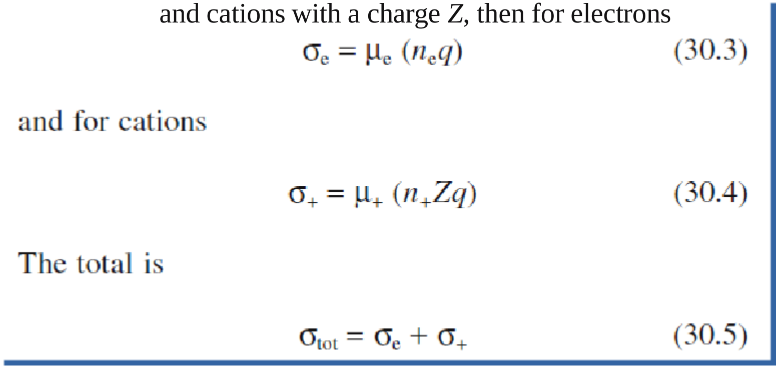
Parameter	*Definition*	*Units/value*	*Conversion factor*
E_g	Band gap energy	eV	1 eV = 1.602×10^{-19} J (eV is a much more convenient unit for E_g)
E_f	Fermi energy		
σ	Conductivity	S/m	1 S = 1 Ω^{-1}
I	Current	A	
J	Current density	$C\,m^{-2}\,s^{-1}$	
v	Drift velocity	m/s	
ξ	Electric field strength	V/m	
μ	Mobility	$m^2\,V^{-1}\,s^{-1}$	Subscripts e and h will be used to represent electron and hole mobility, respectively; the units are the same in both cases
R	Resistance	Ω	
ρ	Resistivity	$\Omega \cdot m$	
V	Voltage	V	
q	Electron charge	1.602×10^{-19} C	Sometimes e
t	Transference number	Dimensionless	
K	Boltzmann constant	1.381×10^{-23} J/K	
T	Temperature	K or °C	
T_c	Critical temperature for superconductivity	K	0 K = –273°C

CONDUCTION MECHANISMS IN CERAMICS

Electrical conductivity is given by:
σ=*n*qμ

The above equation applies to all materials.
Conductivity, σ, depends on two factors Number of charge carriers, *n* and Their mobility, μ

If more than one type of charge carrier is contributing to σ then we can define a partial conductivity for each.
For example, if σ were due to the movement of electrons and cations with a charge *Z*, then for electrons



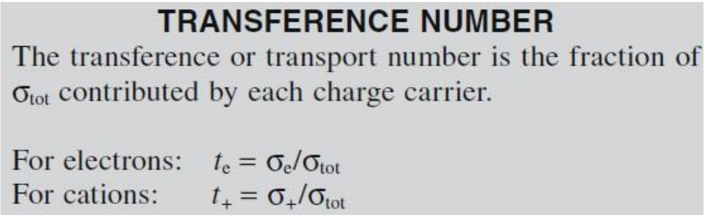
$$\sigma_e = \mu_e\,(n_e q) \tag{30.3}$$

and for cations

$$\sigma_+ = \mu_+\,(n_+ Z q) \tag{30.4}$$

The total is

$$\sigma_{tot} = \sigma_e + \sigma_+ \tag{30.5}$$



TRANSFERENCE NUMBER

The transference or transport number is the fraction of σ_{tot} contributed by each charge carrier.

For electrons: $t_e = \sigma_e/\sigma_{tot}$
For cations: $t_+ = \sigma_+/\sigma_{tot}$

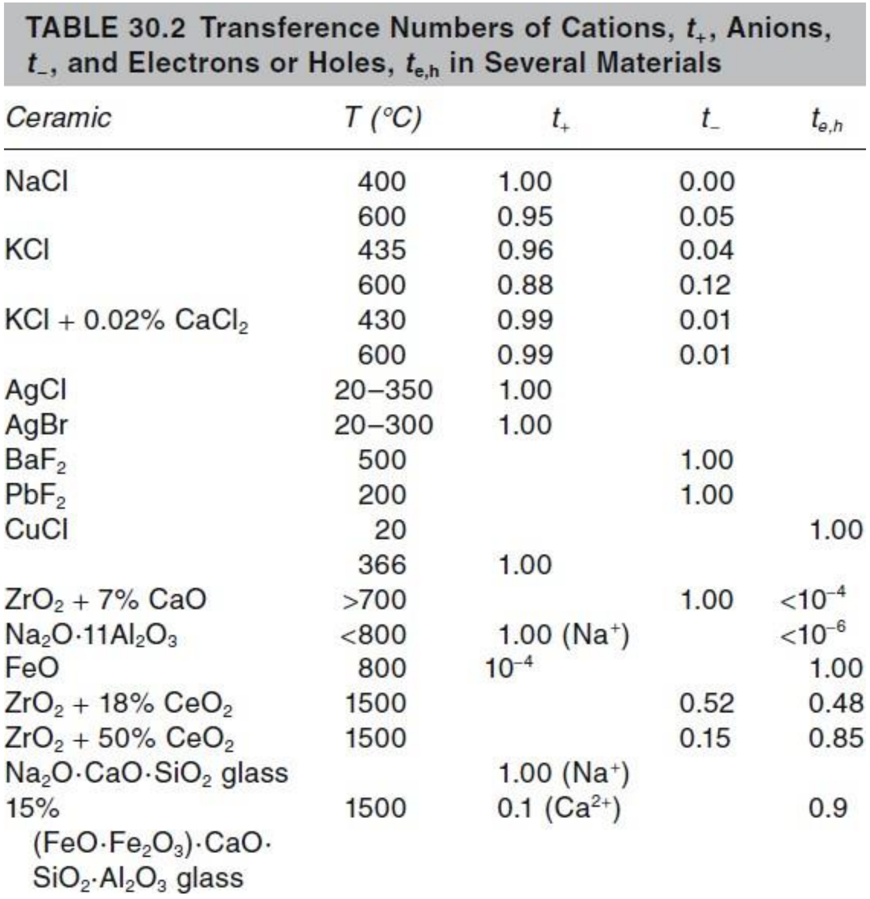
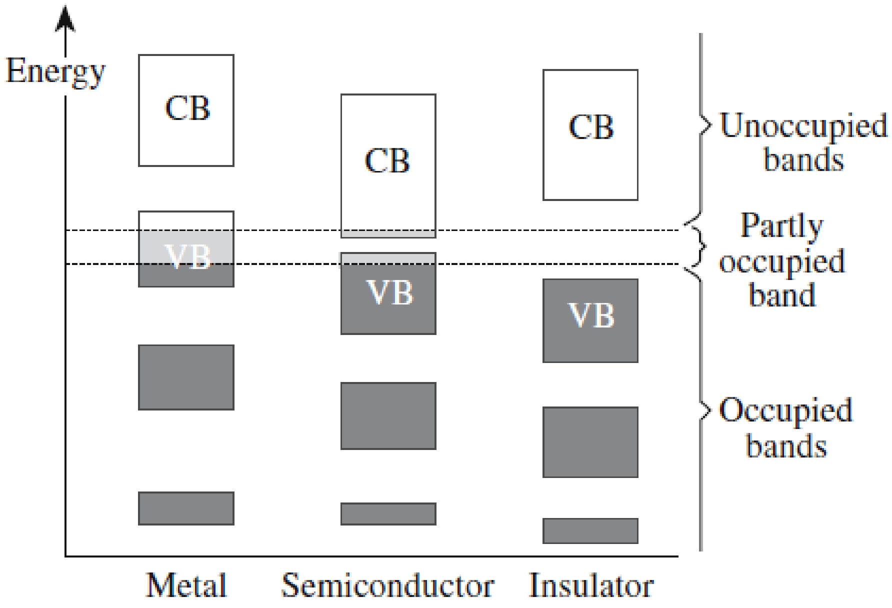


TABLE 30.2 Transference Numbers of Cations, t_+, Anions, t_-, and Electrons or Holes, $t_{e,h}$ in Several Materials

Ceramic	*T (°C)*	t_+	t_-	$t_{e,h}$
NaCl	400	1.00	0.00	
	600	0.95	0.05	
KCl	435	0.96	0.04	
	600	0.88	0.12	
KCl + 0.02% $CaCl_2$	430	0.99	0.01	
	600	0.99	0.01	
AgCl	20–350	1.00		
AgBr	20–300	1.00		
BaF_2	500		1.00	
PbF_2	200		1.00	
CuCl	20			1.00
	366	1.00		
ZrO_2 + 7% CaO	>700		1.00	$<10^{-4}$
$Na_2O\cdot 11Al_2O_3$	<800	1.00 (Na^+)		$<10^{-6}$
FeO	800	10^{-4}		1.00
ZrO_2 + 18% CeO_2	1500		0.52	0.48
ZrO_2 + 50% CeO_2	1500		0.15	0.85
$Na_2O\cdot CaO\cdot SiO_2$ glass		1.00 (Na^+)		
15% $(FeO\cdot Fe_2O_3)\cdot CaO\cdot SiO_2\cdot Al_2O_3$ glass	1500	0.1 (Ca^{2+})		0.9

Band Structure



If a ceramic is an electron conductor, i.e., $t_e = 1$, then to determine n we need to know E_g.
the band gap is either zero, narrow, or wide.
The real band structure of a material is actually a complex three-dimensional shape.

E_g in a metal is not zero, but it is very small. For example, if we have a metal crystal consisting of 10^{23} atoms and the width of the energy band is 1 eV then the separation between the energy levels would be only 10^{-23} eV ($1.6 * 10^{-42}$ J).

A narrow band gap is usually defined as being in the range of 0.02 to about 2.5 eV. When E_g is toward the lowest end of this range there is a significant fraction of electrons in the conduction band.

Materials with a narrow band gap are usually referred to as semiconductors.
Silicon: $E_g = 1.12$ eV
Gallium arsenide: $E_g = 1.42$ eV

Materials with a wide band gap (>2.5 eV) are called wideband- gap semiconductors.

SiC ($E_g = 2.6–3.0$) is an example of a wide-band-gap semiconductor and is used in **sensors** in **aircraft** and **fuel cells** that can operate in hostile environments at temperatures up to 600°C where conventional silicon-based electronics cannot function.

Band Gap Energies for various ceramics

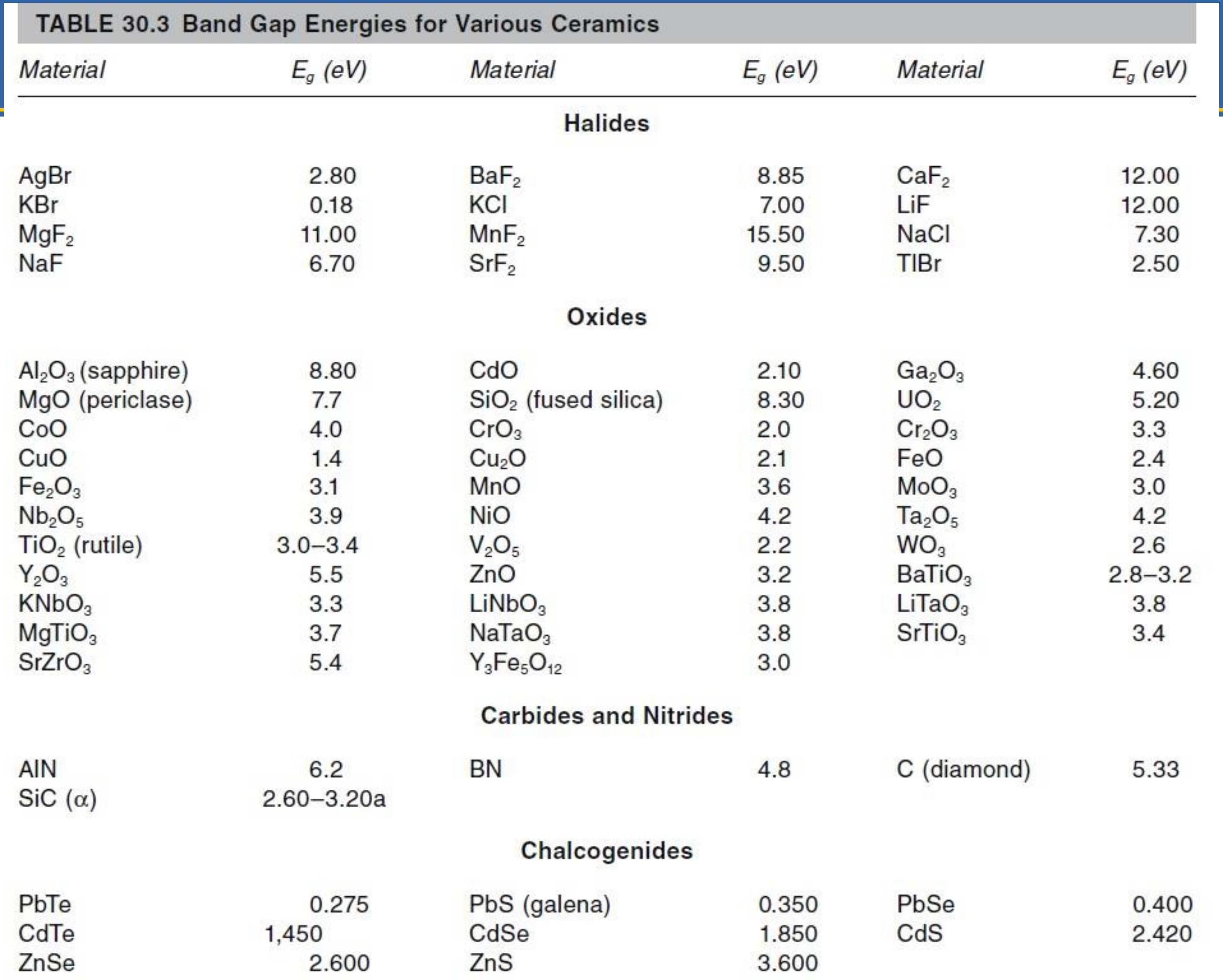


TABLE 30.3 Band Gap Energies for Various Ceramics

Material	E_g (eV)	*Material*	E_g (eV)	*Material*	E_g (eV)
		Halides			
AgBr	2.80	BaF_2	8.85	CaF_2	12.00
KBr	0.18	KCl	7.00	LiF	12.00
MgF_2	11.00	MnF_2	15.50	NaCl	7.30
NaF	6.70	SrF_2	9.50	TlBr	2.50
		Oxides			
Al_2O_3 (sapphire)	8.80	CdO	2.10	Ga_2O_3	4.60
MgO (periclase)	7.7	SiO_2 (fused silica)	8.30	UO_2	5.20
CoO	4.0	CrO_3	2.0	Cr_2O_3	3.3
CuO	1.4	Cu_2O	2.1	FeO	2.4
Fe_2O_3	3.1	MnO	3.6	MoO_3	3.0
Nb_2O_5	3.9	NiO	4.2	Ta_2O_5	4.2
TiO_2 (rutile)	3.0–3.4	V_2O_5	2.2	WO_3	2.6
Y_2O_3	5.5	ZnO	3.2	$BaTiO_3$	2.8–3.2
$KNbO_3$	3.3	$LiNbO_3$	3.8	$LiTaO_3$	3.8
$MgTiO_3$	3.7	$NaTaO_3$	3.8	$SrTiO_3$	3.4
$SrZrO_3$	5.4	$Y_3Fe_5O_{12}$	3.0		
		Carbides and Nitrides			
AlN	6.2	BN	4.8	C (diamond)	5.33
SiC (α)	2.60–3.20a				
		Chalcogenides			
PbTe	0.275	PbS (galena)	0.350	PbSe	0.400
CdTe	1,450	CdSe	1.850	CdS	2.420
ZnSe	2.600	ZnS	3.600		

ELECTRON MOBILITY AND SCATTERING MECHANISMS

As electrons move through a solid under the influence of ξ they experience a number of collisions (in a process called scattering) that decreases μ. There are three scattering mechanisms:

Phonon. This is the major factor affecting μ (of both electrons and holes). A phonon is the quantum unit of lattice vibrational energy.
The higher the temperature the greater the vibrational amplitude of the atoms in the lattice and the greater the number of phonons. As a result, scattering increases and μ decreases with increasing temperature.

$$\mu \propto T^{-m}$$

Electron–electron. At room temperature the mean distance between electron–electron collisions is about 10 times that of electron–phonon collisions so electron– phonon scattering is dominant.

Polaron. This mechanism occurs only in ionic crystals and involves the interaction between the electron and the ions in the crystal. The electron can cause local distortion of the lattice known as a polaron as illustrated in Figure When the interaction is sufficiently strong (small polaron) the electron may be trapped at a particular lattice site, reducing μ and decreasing σ.

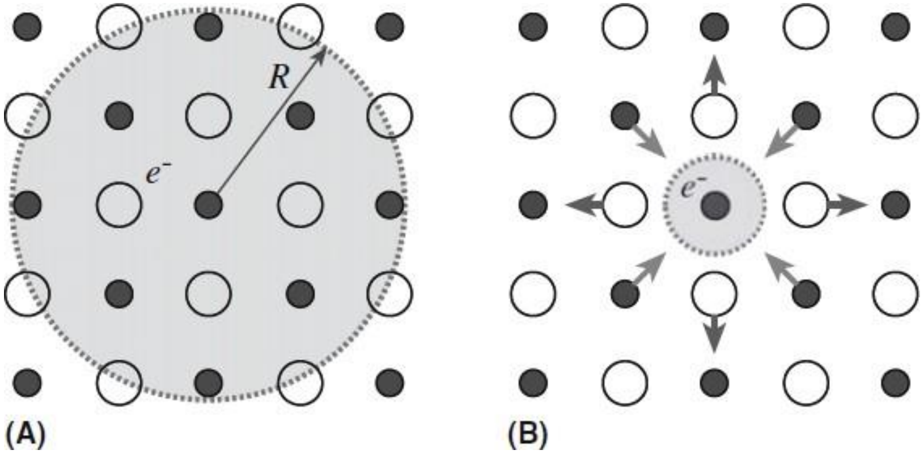


Illustration of (a) a large polaron of radius *R*, formed in a metal oxide MO and (b) a small polaron, showing the distortion of the lattice around an electron trapped at a metal.

EFFECT OF TEMPERATURE

For a material where $E_g = 0$, i.e., one in which n does not vary significantly with T, σ decreases with increasing temperature because of the decrease in μ: $\sigma \propto n / T^m$

For materials where $E_g > 0$ (semiconductors or insulators), σ rises with T because of the temperature dependence of n as shown by

$$\sigma \ \alpha \ EXP(-E/2kT) \text{ ------ } (1)$$

Because it is possible to make practical use of the variation in σ or ρ with T it is often beneficial to classify materials based on this variation. (From a practical point of view we usually consider changes in ρ rather than changes in σ.) The temperature dependence of resistivity may be expressed by an empirical equation

$$\rho_2 = \rho_1[1 + \alpha_R(T_2 - T_1)]$$

where ρ_1 is the resistivity at T_1 and ρ_2 is the resistivity at T_2.

The parameter α_R is known as the temperature coefficient of resistivity or TCR. For materials where $E_g = 0$ the TCR is typically positive. These materials are called positive temperature coefficient (**PTC**) materials.

Most materials that show semiconducting or insulating properties are negative temperature coefficient (**NTC**) materials.
Exceprion: $BaTiO_3$, that do have energy band gaps is actually **PTC** material. This type of behavior has nothing to do with conduction across the band gap but is actually a grain boundary (GB) effect.

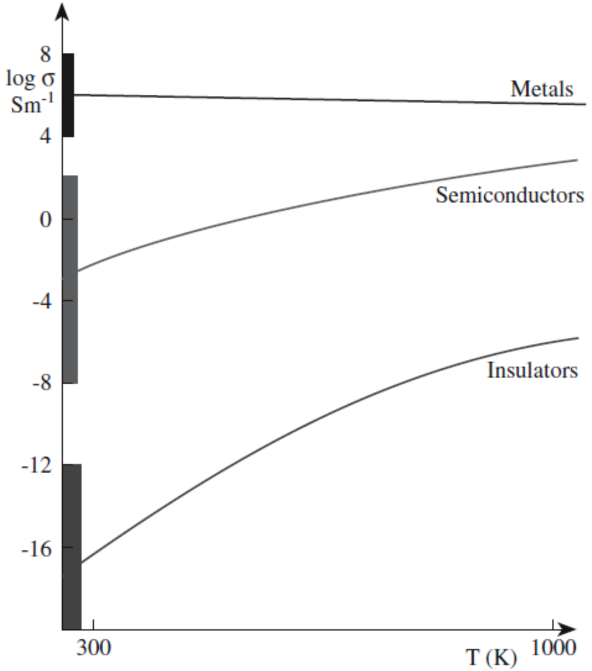


FIGURE 30.4 Conductivity variations with temperature for the different classes of electrical conductor. The shading indicates the range of values at room temperature.

CERAMICS WITH METAL-LIKE CONDUCTIVITY: TiO

The general electrical characteristics of metals are: $\sigma \geq 10^4$ S/m
$t_e = 1$
$n = 10^{22}–10^{23} \text{cm}^{-3}$
$d\sigma/dT$ is small and negative.

Some ceramics, for example TiO and VO, show metallic like electronic conductivity where the conduction is due to the movement of free electrons.

TiO: rocksalt structure with vacancies in both the metal and oxygen sublattices. One-sixth of the titaniums and one-sixth of the oxygens are missing as illustrated in Figure 30.5.

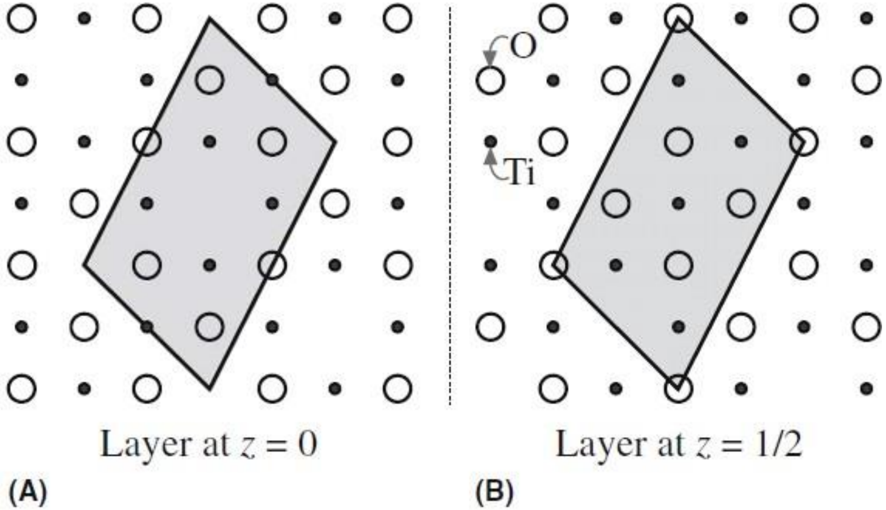
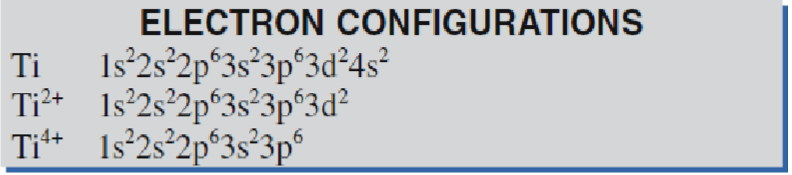


FIGURE 30.5 The structure of TiO. (a) The (100) plane. (b) The (200) plane. Both show the absence of alternate ions along <110> directions. The resultant superlattice has a monoclinic unit cell as indicated by the shaded region.

Band Structure of TiO



ELECTRON CONFIGURATIONS

Ti	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^2 4s^2$
Ti^{2+}	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^2$
Ti^{4+}	$1s^2 2s^2 2p^6 3s^2 3p^6$

The 2p orbitals from the oxygen atoms form a filled valence band. The bands formed by the 4s and 4p orbitals on the Ti are at a much higher energy.

The metal d orbitals form a band below that of the metal s and p orbitals.

The divalent titanium ion, Ti^{2+}, in TiO has two 3d electrons and so the metal d band is partially filled.

This partially filled band resembles the energy level diagram for a metal , resulting to metallic-like conductivity in TiO.

why Titanium dioxide, TiO_2, is an insulator?

In the formation of the Ti^{4+} ion, both the two 4s electrons and the two 3d electrons are given up to form oxygen ions.

So the 3d band (the conduction band in the solid) is empty at $T = 0$ K. The band gap, E_g, in TiO_2 is 3 eV.

This is a relatively small E_g for an insulator and indicates some covalent character in the Ti–O bond

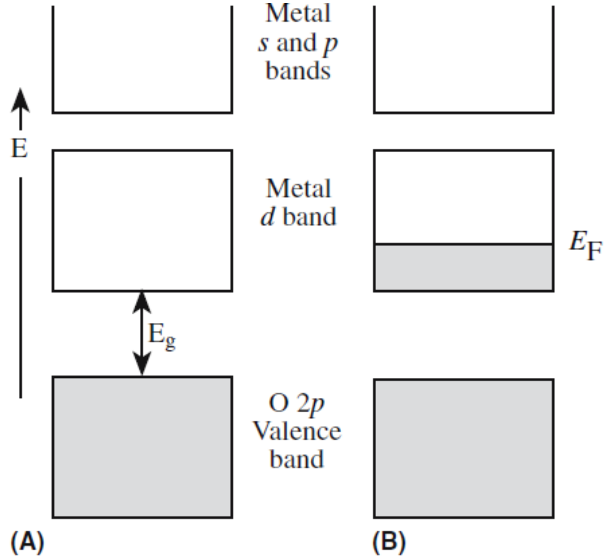


FIGURE 30.6 Energy bands of a transition metal oxide: (a) d band empty; (b) metallic oxide with d band partially filled.

SEMICONDUCTING CERAMICS

Semiconductors have a small E_g

In semiconductors σ is proportional to *n* and μ (for both electrons and holes).

In general, there are three ways free electrons and holes may be generated in ceramics:

Excitation across the band gap (*intrinsic* semiconductors)

Introduction of impurities/dopants (*extrinsic* semiconductors)

Departures from stoichiometry (*nonstoichiometric* semiconductors)

Most oxide semiconductors are either doped to create extrinsic defects or are annealed under conditions in which they become nonstoichiometric.

Intrinsic Semiconductors

For every electron that is excited into the conduction band, a hole is produced in the valence band.

$$\text{The number of electrons in the conduction band is:}$$

$$n = N_c \exp\left(-\frac{E_g}{2kT}\right)$$

$$\text{Similarly, the number of holes in the valence band is:}$$

$$p = N_v \exp\left(-\frac{E_g}{2kT}\right)$$

$$\text{the densities of states are given by:}$$

$$N_c = 2\left(\frac{2um^*_e kT}{h^2}\right)^{3/2} \quad \text{and}$$

$$N_h = 2\left(\frac{2um^*_h kT}{h^2}\right)^{3/2}$$

where m^*_e and m^*_h are the effective masses of the electrons and holes, respectively.

For many ceramics m^*_e and m^*_h are not known and we make the (often incorrect) assumption that $m_e = m^*_e = m^*_h$, where m_e is the rest mass of the electron.

If we use the subscript i to denote intrinsic carrier concentrations, we can write

$$n_i = p_i$$

$$np = n_i p_i = n_i^2$$

$$n_i = (N_c N_v)^{1/2} \exp\left(\frac{-E_g}{2} kT\right)$$

$$\text{if } N_c = N_v \text{ then}$$

$$n_i = N_c \exp\left(\frac{-E_g}{2kT}\right)$$

$$\text{The intrinsic conductivity is given by}$$

$$\sigma_i = q n_i (\mu_e + \mu_h)$$

The intrinsic conductivity of many pure oxide semiconductors is generally very low because of their large E_g compared to Si and GaAs.

Applications of Intrinsic Semiconductors

X-ray detectors used on transmission electron microscopes (TEMs) and scanning electron microscopes (SEMs) for chemical analysis. Unfortunately it is essentially impossible to produce pure silicon.

Even electronic grade silicon contains small amounts of boron (a p-type dopant). To create “intrinsic” material a dopant is added that produces an excess of electrons that combine with the holes formed by the residual boron. The process involves diffusing lithium atoms into the semiconductor. Ionization of the lithium produces electrons that recombine with the holes.

It is possible to produce germanium crystals with much higher purity, and intrinsic Ge detectors are used on some TEMs.

Extrinsic and Nonstoichiometric Semiconductors

An extrinsic semiconductor contains impurities that are present either accidentally or, as is most often the case, that have been intentionally added.

Acceptor: Impurity level is just above the valence band. It can accept electrons leaving holes in the valence band.
Donor: Impurity just below the conduction band edge and can supply electrons into the conduction band.

n-type semiconductor: electrons are the majority carriers
p-type semiconductor: holes are the majority carriers

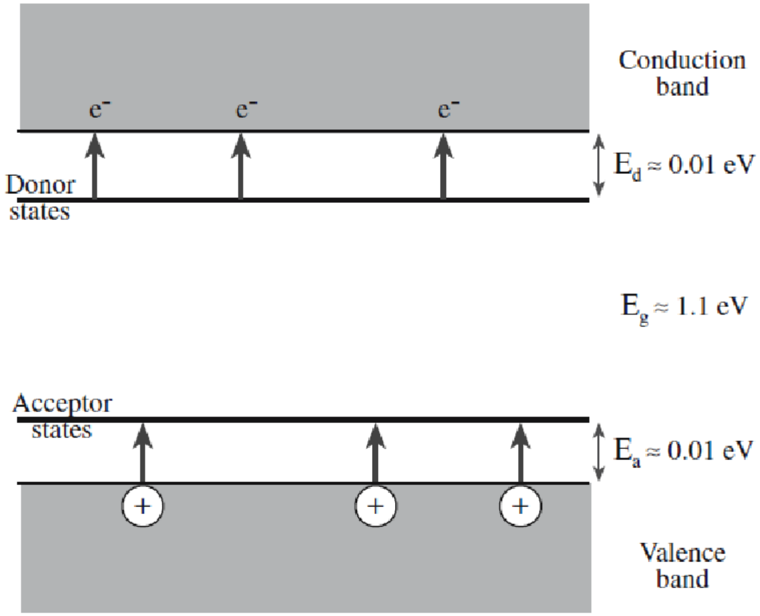


FIGURE 30.11 Effect of doping on band structure.

Extrinsic and Nonstoichiometric Semiconductors

At low T number of charge carriers is determined by the donor and acceptor ionization energies.

At sufficiently high temperatures full ionization of the impurities is achieved and the carrier densities become independent of temperature. This region is called the “exhaustion” or “saturation” region.

At even higher temperatures the thermal energy is enough to excite electrons across the energy band gap and the material behaves like an intrinsic semiconductor.

Nonstoichiometric semiconductors are very similar to extrinsic semiconductors, and can really be considered together. The main difference is that the electronic defects rather than being due to impurity atoms are the result of changes in the stoichiometry of the crystal.

We still use the designations n- and p-type to describe the majority charge carrier and the defect adds levels into the band gap that lead to increased levels of conductivity, particularly at room temperature and below.

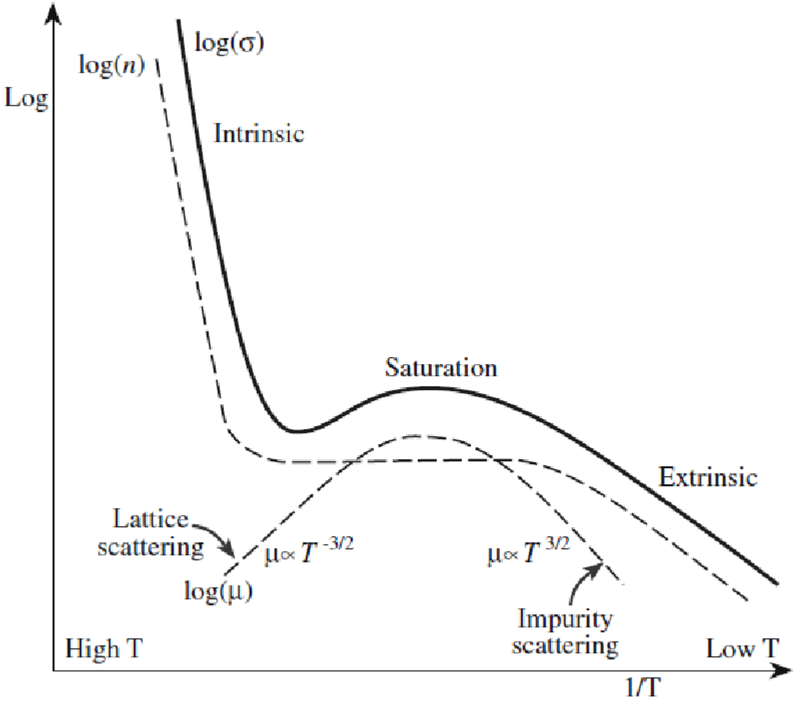


FIGURE 30.12 Temperature dependence of σ for an extrinsic semiconductor. The dashed lines show the individual contributions of *n* and μ to σ.

ION CONDUCTION

Ion movement can make a major contribution to σ, particularly if the material has a large E_g.

Conductivity resulting from ion migration is important in several ceramics.

It is also the major conduction mechanism in ionic salts such as the halides.

When we describe the mobility of ions we often use the absolute mobility, B:

$$B = v/F = v/zeE$$

where v is the drift velocity and F is the applied force (which in this case is the electrical potential, i.e., $F = Zq\xi$, where Z is the charge on the ion.)

B is related to μ: $\mu = ZqB$

$$\sigma = nZq^2B$$

The absolute mobility, and hence σ, is directly related to the diffusion coefficient, D, through the Nernst–Einstein Equation: $D = kTB$

The diffusion coefficient is given by an Arrhenius equation, which means that there is an activation energy that must be overcome for the ions to move through the material.

then σ in terms of D : $\sigma = ne^2D/kT$

The following factors contribute to ionic mobility:

Size. It is easier to move a small ion than a large one.

Charge. A highly charged ion will polarize, and be polarized by ions of opposite charge as it moves past them. This will increase E_A.

Lattice geometry. Some structures contain channels that facilitate the ion movement. A large number of vacant sites can help.

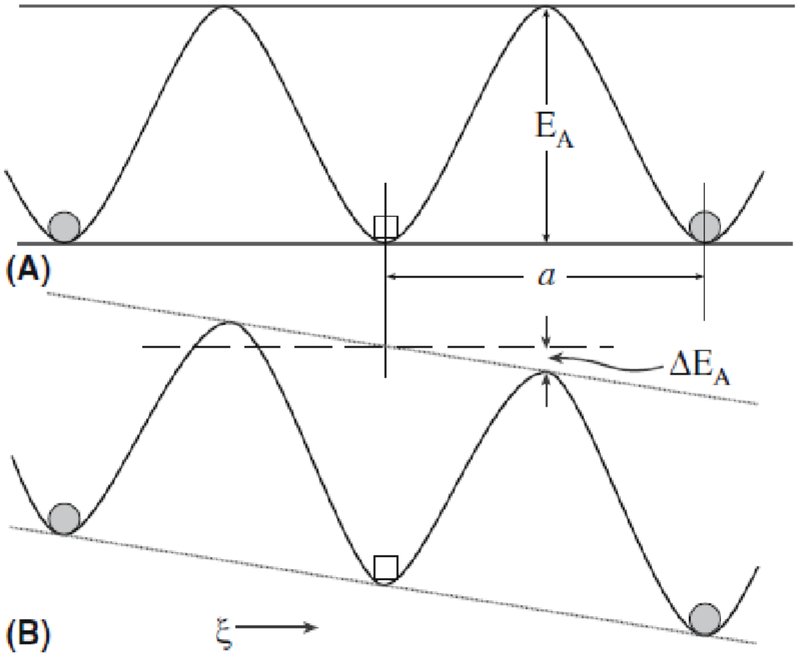


FIGURE 30.20 Potential energy barrier to ion movement. (a) In the absence of an applied field and (b) with an applied field. E_A is the activation energy and a the jump distance between ion sites.

CERAMIC INSULATORS

Many ceramics that have $\rho > 10^{14}\ \Omega\cdot\text{cm}$.

Examples of common ceramic insulators include
Aluminum oxide (Al_2O_3)
Mullite ($3Al_2O_3 \cdot 2SiO_2$)
Forsterite ($2MgO \cdot SiO_2$)
Beryllium oxide (BeO)
Aluminum nitride (AlN)

In an electrical insulator there is a wide energy gap between the bottom of the conduction band and the top of the valence band.

Very wide energy band gaps (>6 eV) are associated with compounds that have high fractions of ionic character in their bonding.

In general, compounds with wide band gaps have Predominantly ionic bonding Consist of atoms (ions) of low Z

In a homologous series of oxides, such as the oxides of the alkaline-earth metals, E_g increases with increasing ionic potential, φ, of the cation.

In a series of isoelectronic compounds (i.e., compounds with an identical total number of electrons) E_g increases

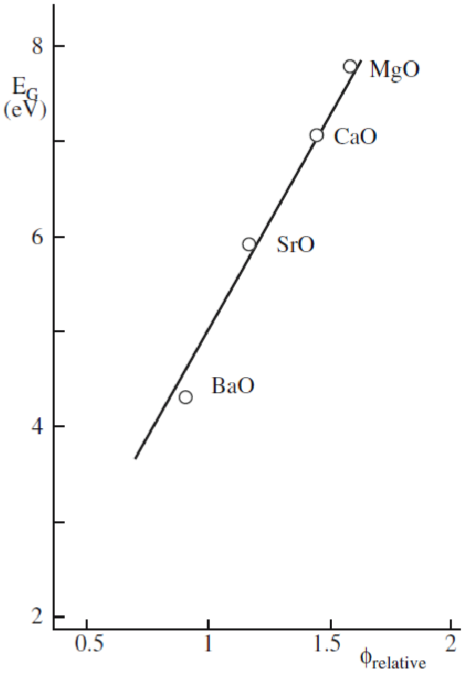


FIGURE 30.24 Effect of bond ionicity on E_g for metal oxides MO ($\phi = Z/r$).

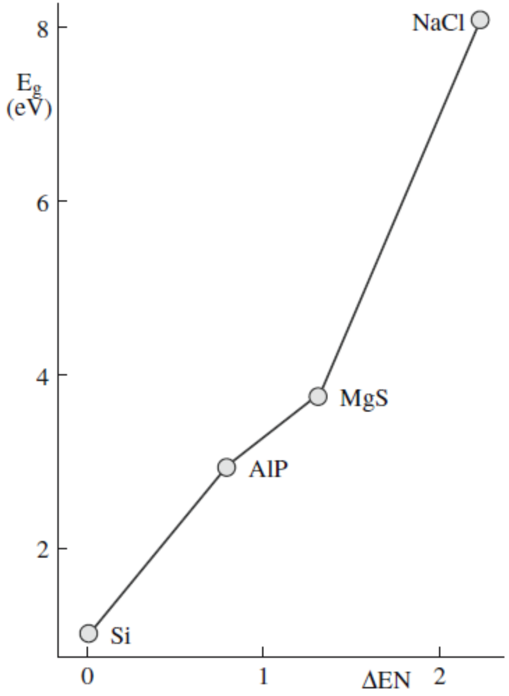


FIGURE 30.25 Correlation of E_g and electronegativity difference (ΔEN).

Ceramic Insulators: Band Diagrams of MgO and Defect (donor) Levels (contd..)

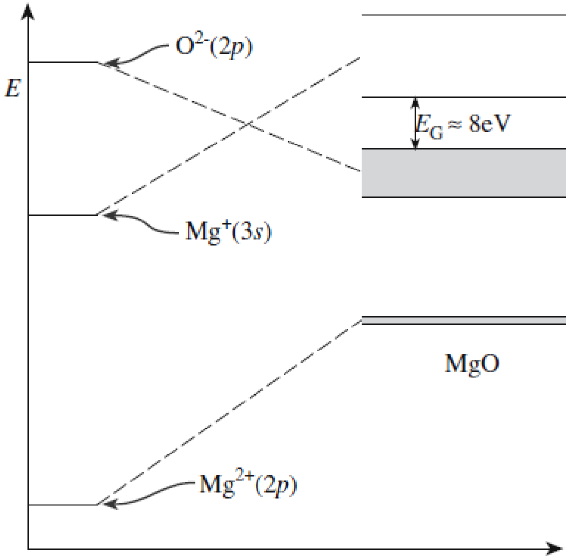


FIGURE 30.23 Energy band diagram for MgO.

shows the energy band diagram for MgO. The valence band is formed by the 2p energy levels of oxygen (O^{2-} ions) and the conduction band is formed from the empty 3s orbitals of the Mg^{2+} ions. The energy band gap is ~8 eV and the concentration of thermally excited electrons in the conduction band of MgO is low right up to its melting point, 2800°C. MgO is therefore an excellent high temperature insulator.

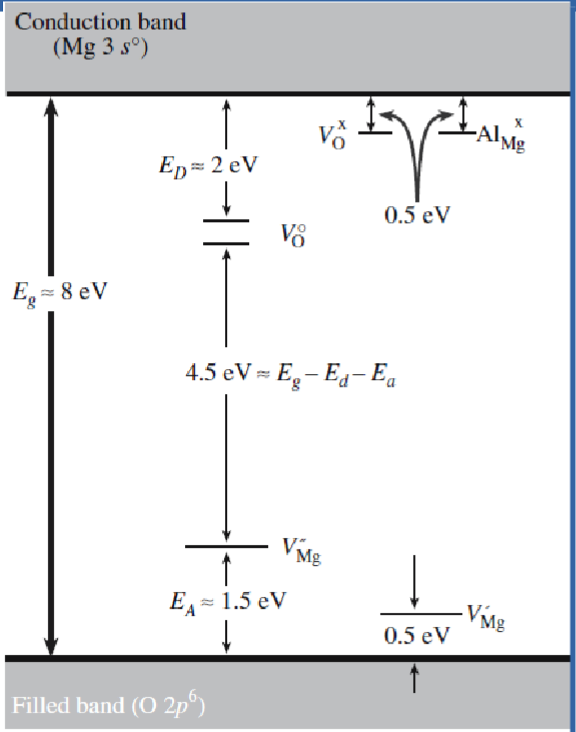


FIGURE 30.26 Defect levels in MgO.

The presence of point defects in the lattice can be viewed as being donor or acceptor species in the same way that we considered defects in semiconductor crystals.

If the crystal contains oxygen vacancies (i.e., it has been reduced) these can become ionized:

The energy for ionization is 0.5 eV and can be represented as a level just below the bottom of the conduction band—**the oxygen vacancy is behaving as a donor.**

$$(V_O^x) \rightarrow (V_O^\bullet) + e'$$

The oxygen vacancy can become doubly ionized:

$$(V_O^\bullet) \rightarrow (V_O^{\bullet\bullet}) + e'$$

The energy for this second ionization process is ~2 eV and can be represented as another donor level.

MgO Band Diagrams: Defect (Acceptor & Substitutional) Levels

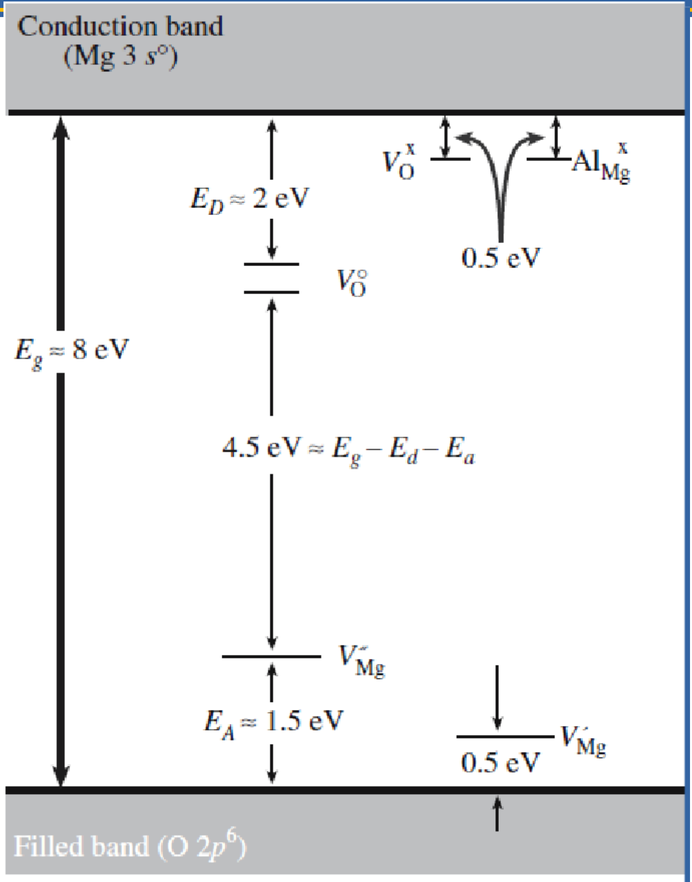


FIGURE 30.26 Defect levels in MgO.

$$(V_{Mg}^x) \rightarrow (V'_{Mg}) + h^\cdot \qquad (30.44)$$

and

$$(V'_{Mg}) \rightarrow (V''_{Mg}) + h^\cdot \qquad (30.45)$$

$$Al_2O_3 \xrightarrow{MgO} 2(Al_{Mg})^\cdot + (3O_O)^x + (V_{Mg})'' \qquad (30.46)$$

and

$$Al_2O_3 \xrightarrow{MgO} 2(Al_{Mg})^\cdot + (O_O)^x + O_2 + 2e' \qquad (30.47)$$

Even though these ionization energies are relatively small compared to the band gap, the concentration of these defects is extremely low.

Even at temperatures >2000°C the number of cation and anion vacancies in MgO is only about one per billion lattice sites.

The addition of substitutional and interstitial point defects can also introduce additional energy levels.

SUBSTRATES AND PACKAGES FOR INTEGRATED CIRCUITS

Substrates and packages for integrated circuits (ICs) constitute the largest application for ceramic insulators.
The following properties are required:

- High ρ
- High thermal conduction
- Low dielectric constant
- Hermetic

Three ceramics are usually used for this application:

- Al_2O_3
- BeO
- AlN

Alumina ceramics dominate, but there are important reasons why BeO and AlN are used in certain applications.

BeO and AlN are used in situations in which high thermal conductivity is needed.

Heat removal from power electronics and from integrated circuits is determined mainly through the substrate;

One factor that influences the heat transfer rate is the thermal conductivity of the substrate material.

Effective thermal management is important in improving the reliability of electronic devices.

AlN has a theoretical thermal conductivity of 320 $\text{Wm}^{-1}\text{K}^{-1}$ and values as high as 285 $\text{Wm}^{-1}\,\text{K}^{-1}$ have been experimentally measured for single crystals.

Commercial AlN substrates are available with a thermal conductivity up to about 200 $\text{Wm}^{-1}\,\text{K}^{-1}$ at RT.

The thermal expansion of AlN ($3.9 \text{ X } 10^{-6}\text{K}^{-1}$) from room temperature to 500 K is very similar to that of silicon ($3 \text{ X } 10^{-6}\text{ K}^{-1}$) over the same temperature interval, which helps to avoid cracking due to thermal misfit stresses between substrate and device.

This consideration is particularly important for large silicon chips.

AlN also does not have the inherent toxicity problems associated with BeO.

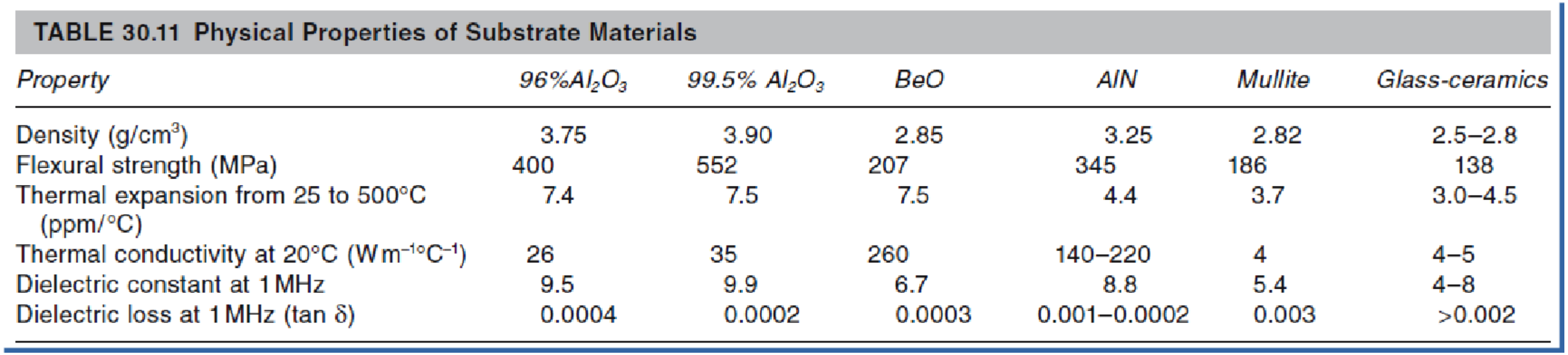


TABLE 30.11 Physical Properties of Substrate Materials

Property	*96%Al_2O_3*	*99.5% Al_2O_3*	*BeO*	*AlN*	*Mullite*	*Glass-ceramics*
Density (g/cm^3)	3.75	3.90	2.85	3.25	2.82	2.5–2.8
Flexural strength (MPa)	400	552	207	345	186	138
Thermal expansion from 25 to 500°C (ppm/°C)	7.4	7.5	7.5	4.4	3.7	3.0–4.5
Thermal conductivity at 20°C ($W m^{-1} {}^\circ C^{-1}$)	26	35	260	140–220	4	4–5
Dielectric constant at 1 MHz	9.5	9.9	6.7	8.8	5.4	4–8
Dielectric loss at 1 MHz (tan δ)	0.0004	0.0002	0.0003	0.001–0.0002	0.003	>0.002

SUPERCONDUCTIVITY

There are two properties that a material must possess to be considered a superconductor:

1. $\rho = 0$
2. $B = 0$

Zero resistivity is observed in a superconductor at all temperatures below a critical temperature, T_c.

At T_c the material changes from a state of normal conduction to the superconducting state - an induced current will flow indefinitely without loss.

This behavior has been demonstrated experimentally when a current has been run through a closed ring of a superconducting metal for over two and a half years without any measurable decay.

Superconductivity has been observed in *all* the classes of materials: metals, ceramics, and polymers.

Of all the elements in the periodic table only 27 are known to become superconducting under ordinary pressure.
Niobium is the element with the highest T_c, 9.2 K, whereas for tungsten T_c is only 0.0154 K.

An interesting fact is that metals having the highest σ, e.g., Cu, Ag, and Au, are not superconducting even at extremely low temperatures, if at all.

It is the metals that are the poorer electrical conductors that make the better superconductors, albeit still at very low temperatures.

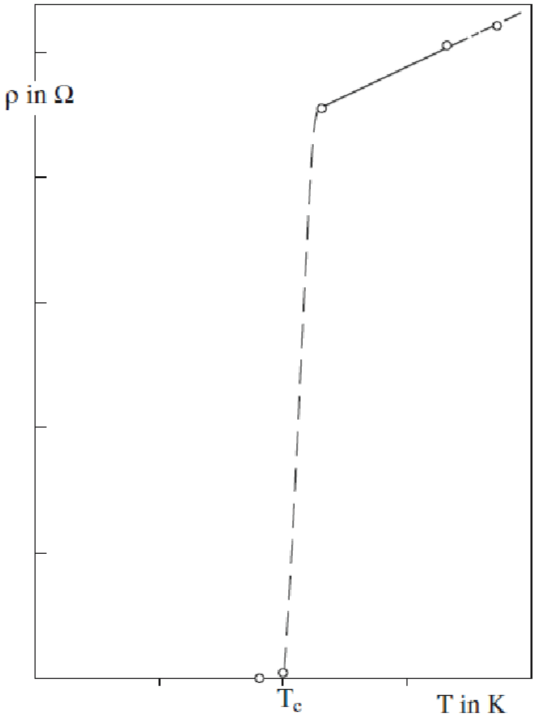


FIGURE 30.28 Plot of ρ versus T for a superconductor.

SUPERCONDUCTIVITY: LTSC & HTSC

Low-temperature superconductors (LTSC) have a T_c up to about 20 K and High-temperature superconductors (HTSC) are usually defined as having a T_c above the boiling temperature of liquid nitrogen.

The BCS theory (after Bardeen, Cooper, and Schrieffer) provides an explanation for superconductivity at low temperatures.

The theory is complicated, but the basis is that there exists an attractive force between electrons that have about the same energy. This force causes them, under the right circumstances, to move in pairs. These are the so-called **Cooper** pairs.

The criterion for superconductivity is that this attraction should be greater than the natural repulsion between like charges. T_c corresponds to the binding energy needed to hold the Cooper pairs together in a superconducting state.

The origin of the attractive force is that in a lattice of positive ions, an electron will attract the positive ions toward itself. In this region the lattice will be slightly denser.

To a passing electron the local lattice distortion will appear as an increase in positive charge density and it will be attracted toward it. The two electrons pair up in this way through their interaction with the lattice.

If the lattice is vibrating through thermal effects pairing will not be possible, but at very low temperatures where the vibration amplitude is small, the attractive force can be dominant. The electrons are held together by a binding energy of only about 10^{-4} eV.

The separation of the electrons in the pair (called the coherence length) for most LTSC is 100 nm. Interatomic spacings are on the order of 0.3 nm, so two bound electrons can be as far apart as 300 lattice spaces.

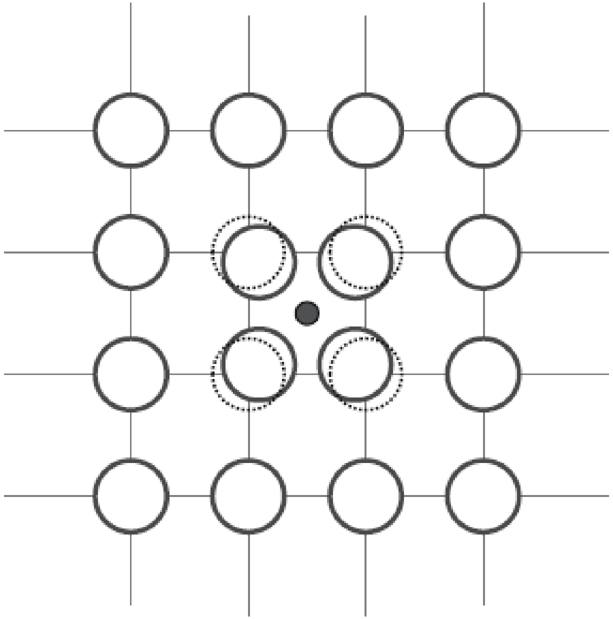


FIGURE 30.29 Illustration of lattice distortion around a free electron, which leads to the formation of Cooper pairs.

SUPERCONDUCTIVITY: Band Structure (contd..)

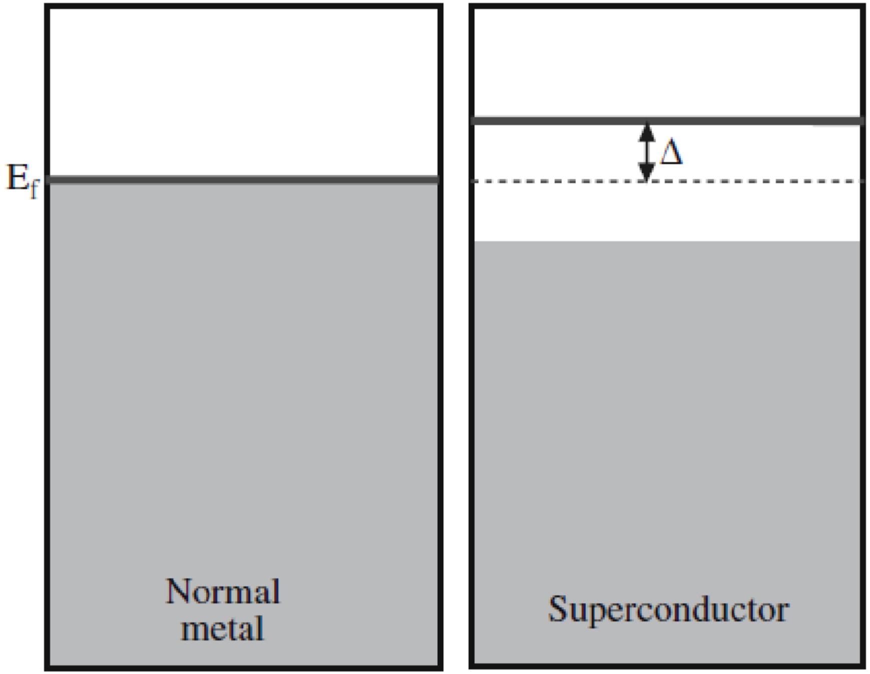


FIGURE 30.30 Band diagram for a superconductor.

The large coherence length means that defects such as dislocations, GBs, and impurities are too small to have much effect on superconducting behavior.

The existence of these bound electron pairs alters the energy band diagram for a superconductor by introducing a small gap at E_F, known as the superconducting gap, Δ.

The energy of this gap corresponds to the binding energy of the electron pairs.
An energy 2Δ is needed to break a Cooper pair.
The relationship between Δ and T_c is given by the BCS theory:
$2\Delta = 3.5\, kT_c$
For LTSC Δ ~1 meV
For HTSC Δ ~1–10 meV
The BCS theory predicts an ultimate limiting value of T_c of 30 K for electron pairing via lattice vibrations (phonons).
But clearly the BCS theory, in its entirety, cannot be applicable to HTSC where T_c >> 30 K.
In these materials pairing of the electrons still occurs, but the mechanism that allows this pairing needs to be determined.

CERAMIC SUPERCONDUCTORS: HTSCs

The earliest non-metallic superconductors : NbO & NbN (rocksalt crystal structure).
Significance of Discovery: **Ceramics** & **Cubic Crystal Structures**.
Superconductivity in a multicomponent oxide was first observed in $SrTiO_3$.

Although T_c = 0.3 K, $SrTiO_3$ has perovskite structure,(structural building block of all presently known HTSC.)
The beginning of HTSC discovery in 1986 : La_2BaCuO_4, which has T_c ~38 K.
Importance of HTSC discovery: BCS theory for superconductivity predicted a maximum value of T_c of only 30 K!
Many more HTSC were simply obtained by systematic substitution of elements into the basic perovskite unit.
The elements yttrium <=> lanthanum are interchangeable and strontium <=> barium.
The idea behind the substitution of the large element for a smaller element
was based on observations that T_c could be raised under an applied pressure.
Substitution of a larger element for a smaller one was thought to produce an internalized pressure effect.

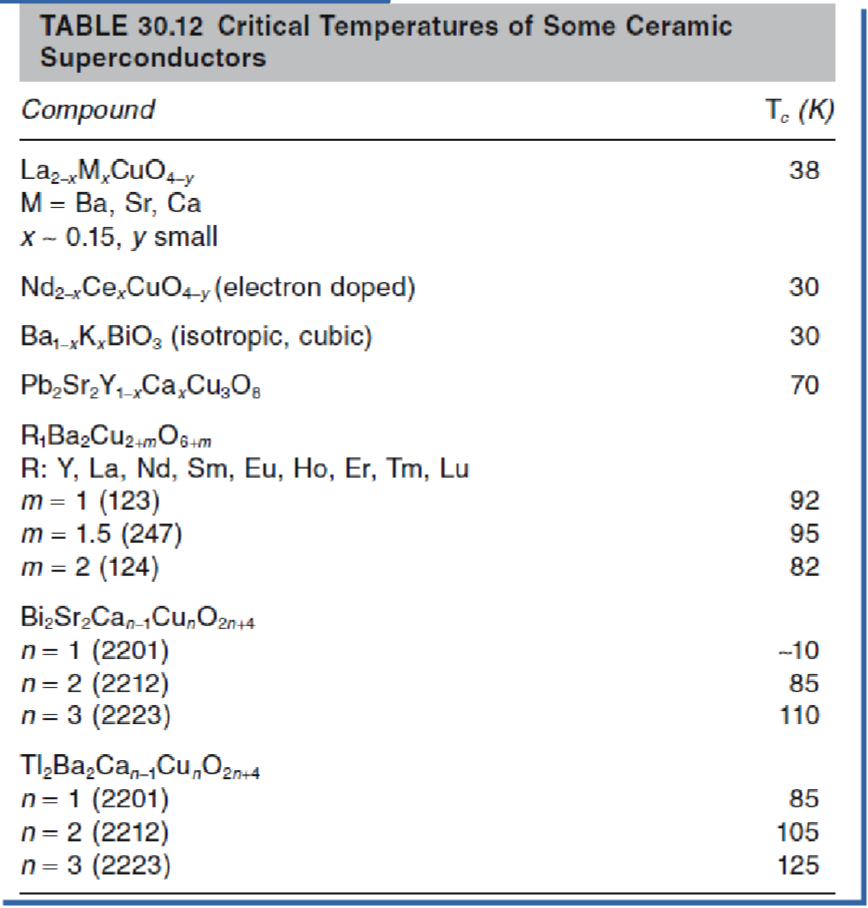


TABLE 30.12 Critical Temperatures of Some Ceramic Superconductors

Compound	T_c *(K)*
$La_{2-x}M_xCuO_{4-y}$ M = Ba, Sr, Ca x ~ 0.15, y small	38
$Nd_{2-x}Ce_xCuO_{4-y}$ (electron doped)	30
$Ba_{1-x}K_xBiO_3$ (isotropic, cubic)	30
$Pb_2Sr_2Y_{1-x}Ca_xCu_3O_8$	70
$R_1Ba_2Cu_{2+m}O_{6+m}$ R: Y, La, Nd, Sm, Eu, Ho, Er, Tm, Lu	
m = 1 (123)	92
m = 1.5 (247)	95
m = 2 (124)	82
$Bi_2Sr_2Ca_{n-1}Cu_nO_{2n+4}$	
n = 1 (2201)	~10
n = 2 (2212)	85
n = 3 (2223)	110
$Tl_2Ba_2Ca_{n-1}Cu_nO_{2n+4}$	
n = 1 (2201)	85
n = 2 (2212)	105
n = 3 (2223)	125

Superconductivity (contd..)

- The obvious difference is T_c. The fact that $T_c \sim 10^2$K means that the binding energy is ~10 meV, as compared to <1 meV in LTSC.
- The ceramics have higher ρ than the metals at 100 K. But ρ is comparable to some of the best ceramic electrical conductors, such as CrO_2 and TiO.
- For HTSC χ is only ~1.0 nm, which means that the pairing behavior is almost on an atomic scale and the superconducting properties will be dependent on atomic scale defects. (Compare χ with the width of a dislocation or GB.) Such defects therefore scatter the electron pairs and reduce the critical current density.
- For metals χ is large, e.g., χ = 1.6 μm in pure Al, χ = 38 nm in pure Nb.
- χ is anisotropic. For YBCO $\chi_{ab} \sim 1.5$ nm and $\chi_c \sim 0.4$ nm. A major problem in HTSC is to find a crystal defect that pins the flux vortices, but does not disrupt current flow.

Superconductivity essentially takes place within the CuO_2 planes. The Cu–O chains can be considered as a “charge reservoir” that is needed to transfer charge into the CuO_2 planes.
Charge carriers are added by doping: adding oxygen to $YBa_2Cu_3O_6$, which enters the compound as O^{2-} and forms Cu–O chains.
To maintain charge balance, electrons are removed from the Cu–O planes and the remaining holes are mobile (hence conduction) and form Cooper pairs below T_c.
In LTSC Cooper pairs, with a charge of −2e, are responsible for current flow.
In most of the HTSC the Cooper pairs have a positive charge, +2e. In other words they are positive holes and the charge transfer process can be written as $Cu^{2+} + h^+ \rightarrow Cu^{3+}$.

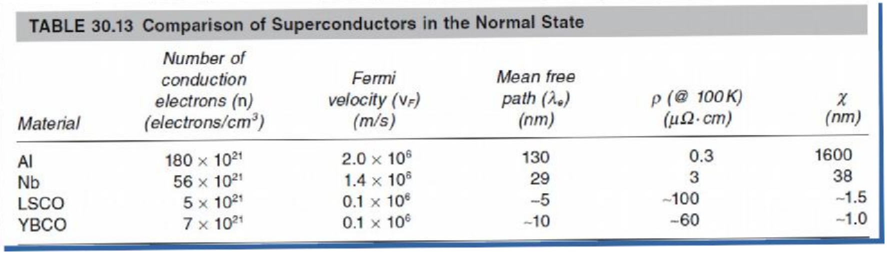


TABLE 30.13 Comparison of Superconductors in the Normal State

Material	Number of conduction electrons (n) (electrons/cm^3)	Fermi velocity (v_F) (m/s)	Mean free path (λ_e) (nm)	ρ (@ 100 K) (μΩ·cm)	χ (nm)
Al	180×10^{21}	2.0×10^6	130	0.3	1600
Nb	56×10^{21}	1.4×10^6	29	3	38
LSCO	5×10^{21}	0.1×10^6	~5	~100	~1.5
YBCO	7×10^{21}	0.1×10^6	~10	~60	~1.0

One of the consequences of a hole-hopping process involving a two-dimensional array of copper ions is that the superconducting current is very anisotropic. Hopping tends to occur between copper ions that have the smallest separation from each other, namely those in the plane. The distance between copper ions on adjacent planes is muchlarger than within the planes; hence charge hopping between planes is much less efficient.

Superconductors: Josephson Junction

The original observation of this effect was made using a junction consisting of two superconductors separated by a very thin insulating layer (~1 nm). In thin films the "insulating" region can be orientation changes across a GB.

The *I*–*V* characteristics of a Josephson junction are very nonlinear. The key features are as follows:

When $V = 0$, a direct current flows.

When a small voltage is applied $I = 0$.

At V_c the electrons are no longer paired and normal electron tunneling occurs with associated resistive losses.

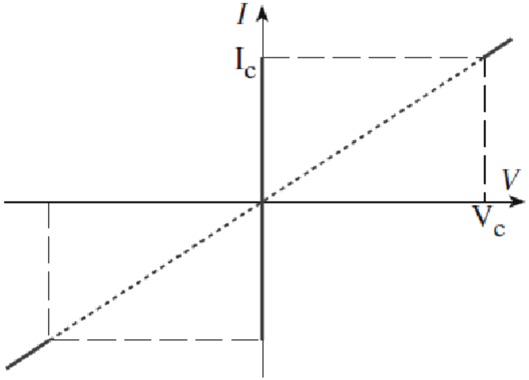


FIGURE 30.31 *I*–*V* characteristics of a Josephson junction.

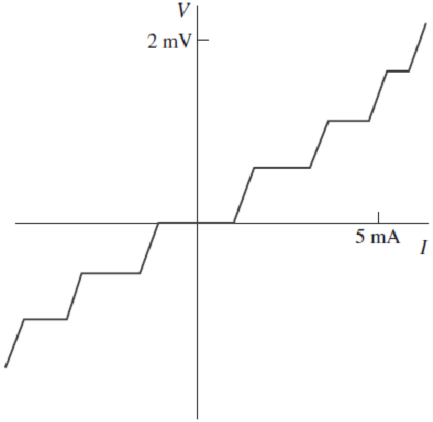


FIGURE 30.32 Effect of incident microwave radiation on the *I*–*V* characteristics of a Josephson junction.

If a Josephson junction is irradiated with microwaves of frequency *f*, the *I*–*V* behavior shows a series of steps, called Shapiro steps. These steps correspond to supercurrents across the junction when the condition for the absorption of microwave photons is satisfied (this is called the ac-Josephson effect). Similar behavior is seen when we expose the junction to a magnetic field. Josephson junctions can be used to detect very small magnetic fields.