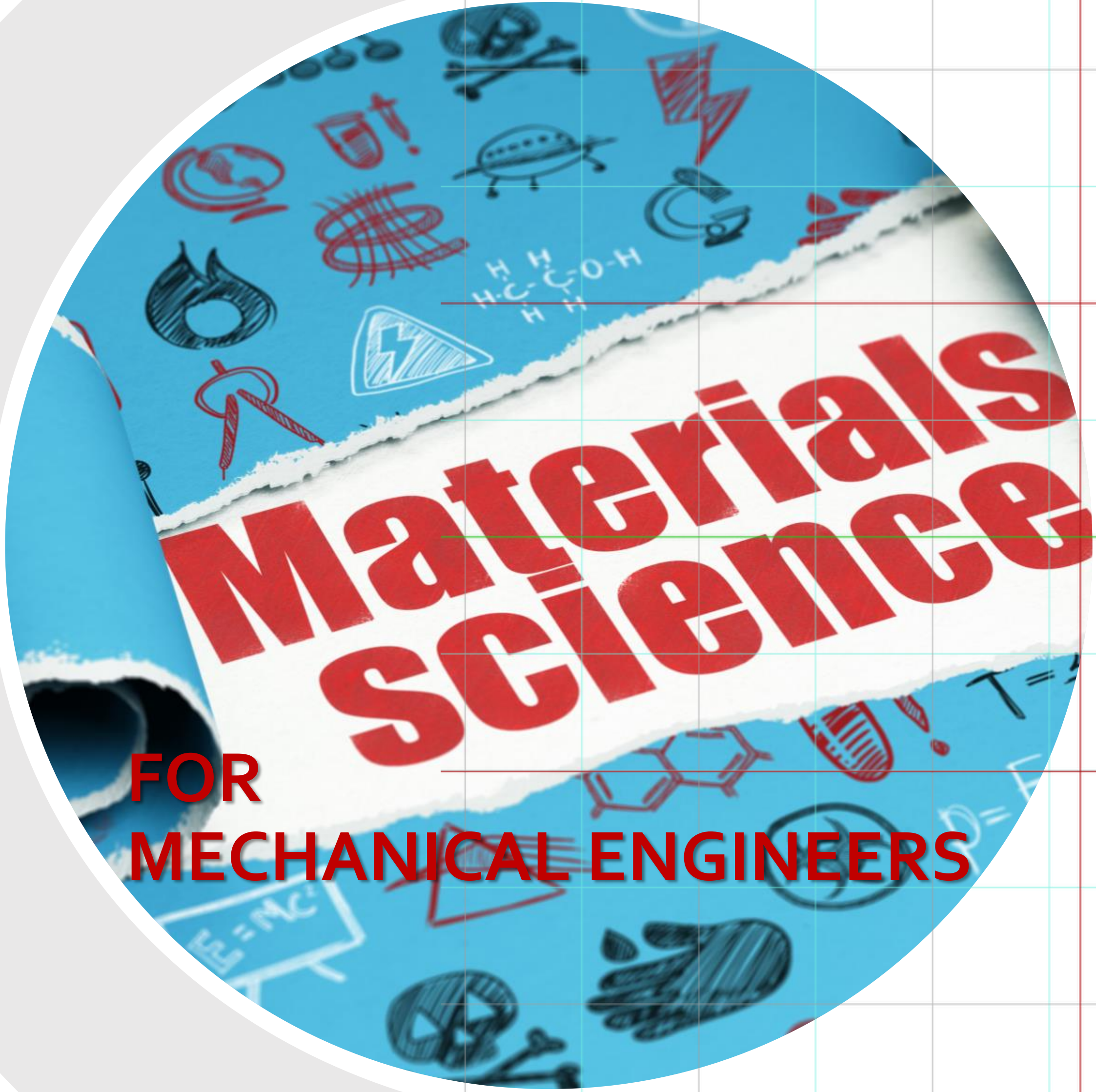


FOR
MECHANICAL ENGINEERS

Structures and Properties of Ceramics

SPRING 2022-2023

INTRODUCTION

Ceramic materials are inorganic and nonmetallic materials. Most ceramics are compounds between metallic and nonmetallic elements for which the interatomic bonds are either totally ionic, or predominantly ionic but having some covalent character.

The term *ceramic* comes from the Greek word *keramikos*, which means “burnt stuff,” indicating that desirable properties of these materials are normally achieved through a high-temperature heat treatment process called firing.

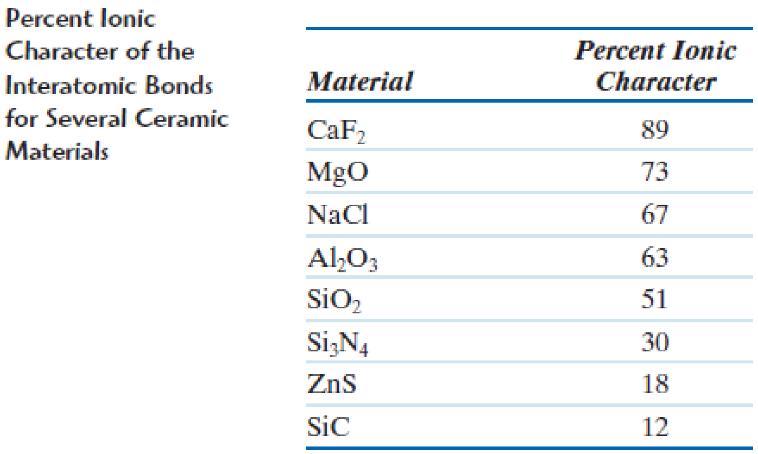
Up until the past 60 or so years, the most important materials in this class were termed the “traditional ceramics,” those for which the primary raw material is clay; products considered to be traditional ceramics are china, porcelain, bricks, tiles, and, in addition, glasses and high-temperature ceramics.

INTRODUCTION

Ceramic Structures

Because ceramics are composed of at least two elements, and often more, their crystal structures are generally more complex than those for metals.

The atomic bonding in these materials ranges from purely ionic to totally covalent; many ceramics exhibit a combination of these two bonding types, the degree of ionic character being dependent on the electronegativities of the atoms.



Percent Ionic Character of the Interatomic Bonds for Several Ceramic Materials

Material	*Percent Ionic Character*
CaF_2	89
MgO	73
NaCl	67
Al_2O_3	63
SiO_2	51
Si_3N_4	30
ZnS	18
SiC	12

Quiz

Calculate the % Ionic Character for the following Ceramic Materials:

CaF_2
MgO
$NaCl$
Al_2O_3
SiO_2
Si_3N_4
ZnS
SiC

INTRODUCTION

CRYSTAL STRUCTURES

For those ceramic materials for which the atomic bonding is predominantly ionic, the crystal structures may be thought of as being composed of electrically charged ions instead of atoms.

The metallic ions, or **cations,** are positively charged because they have given up their valence electrons to the nonmetallic ions, or **anions,** which are negatively charged.

Two characteristics of the component ions in crystalline ceramic materials influence the crystal structure: the magnitude of the electrical charge on each of the component ions, and the relative sizes of the cations and anions.

With regard to the first characteristic, the crystal must be electrically neutral; that is, all the cation positive charges must be balanced by an equal number of anion negative charges. The chemical formula of a compound indicates the ratio of cations to anions, or the composition that achieves this charge balance.

INTRODUCTION

For example, in calcium fluoride, each calcium ion has a +2 charge (Ca^{2+}), and associated with each fluorine ion is a single negative charge (F^{-}). Thus, there must be twice as many F^{-} as Ca^{2+} ions, which is reflected in the chemical formula CaF_2.

The second criterion involves the sizes or ionic radii of the cations and anions, r_C and r_A, respectively.

Because the metallic elements give up electrons when ionized, cations are ordinarily smaller than anions, and, consequently, the ratio r_C/r_A is less than unity. Each cation prefers to have as many nearest-neighbor anions as possible.

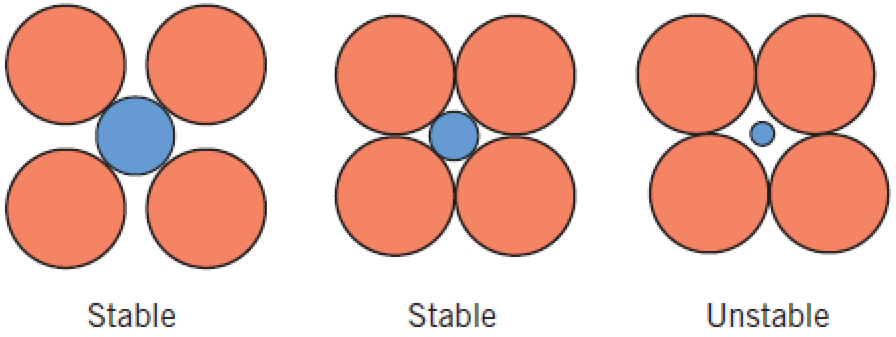
The anions also desire a maximum number of cation nearest neighbors.

INTRODUCTION

Stable ceramic crystal structures form when those anions surrounding a cation are all in contact with that cation.

The coordination number (i.e., number of anion nearest neighbors for a cation) is related to the cation–anion radius ratio. For a specific coordination number, there is a critical or minimum ratio for which this cation–anion contact is established; this ratio may be determined from pure geometrical considerations.

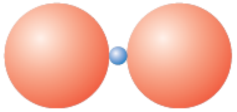
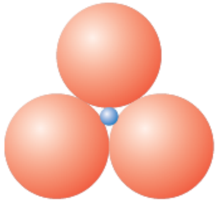
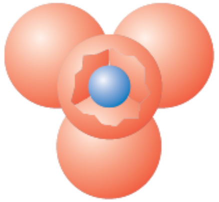
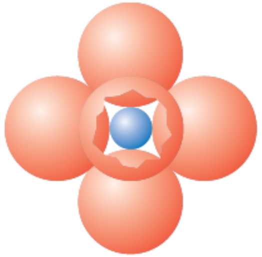
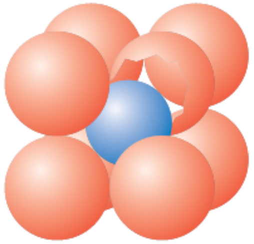
Stable and unstable cation–anion coordination configurations. Red circles represent anions; blue circles denote cations.



INTRODUCTION

The coordination numbers and nearest-neighbor geometries for various ratios are presented in. For ratios less than 0.155, the very small cation is bonded to two anions in a linear manner. If *the ratio* has a value between 0.155 and 0.225, the coordination number for the cation is 3. This means each cation is surrounded by three anions in the form of a planar equilateral triangle, with the cation located in the center.

The coordination number is 4 for *ratio* between 0.225 and 0.414; the cation is located at the center of a tetrahedron, with anions at each of the four corners.

Coordination Number	*Cation–Anion Radius Ratio*	*Coordination Geometry*
2	<0.155	
3	0.155–0.225	
4	0.225–0.414	
6	0.414–0.732	
8	0.732–1.0	

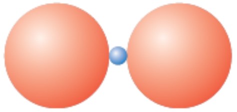
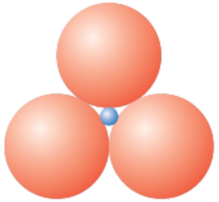
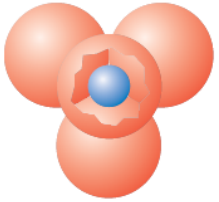
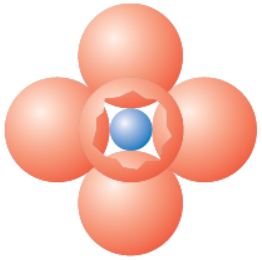
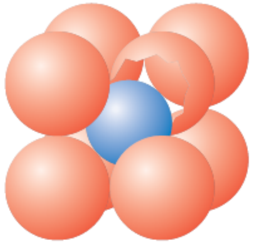
INTRODUCTION

For *ratio* between 0.414 and 0.732, the cation may be thought of as being situated at the center of an octahedron surrounded by six anions, one at each corner, as also shown in the table.

The coordination number is 8 for *Ratio* between 0.732 and 1.0, with anions at all corners of a cube and a cation positioned at the center.

For a radius ratio greater than unity, the coordination number is 12.

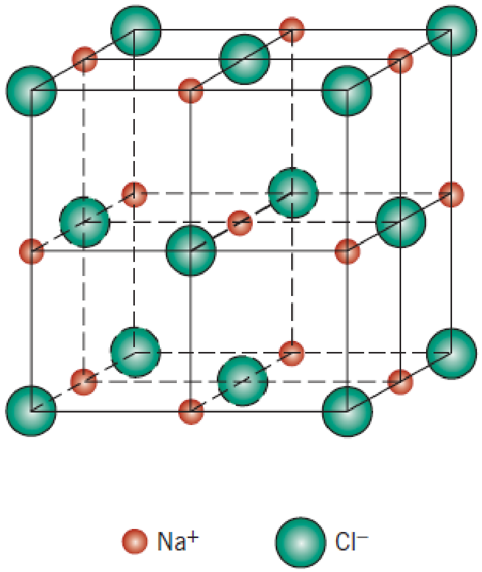
The most common coordination numbers for ceramic materials are 4, 6, and 8.

Coordination Number	*Cation–Anion Radius Ratio*	*Coordination Geometry*
2	<0.155	
3	0.155–0.225	
4	0.225–0.414	
6	0.414–0.732	
8	0.732–1.0	

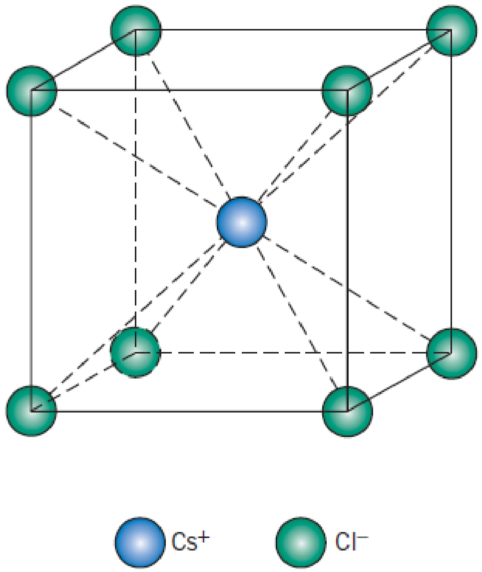
INTRODUCTION

AX-Type Crystal Structures

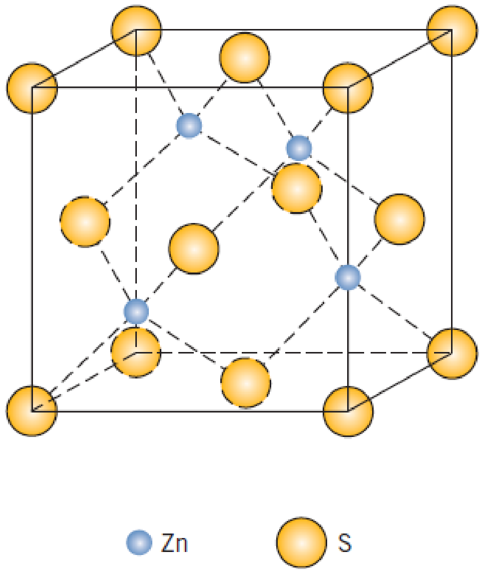
Some of the common ceramic materials are those in which there are equal numbers of cations and anions. These are often referred to as AX compounds, where A denotes the cation and X the anion. There are several different crystal structures for AX compounds; each is typically named after a common material that assumes the particular structure.



A unit cell for the rock salt, or sodium chloride (NaCl), crystal structure.

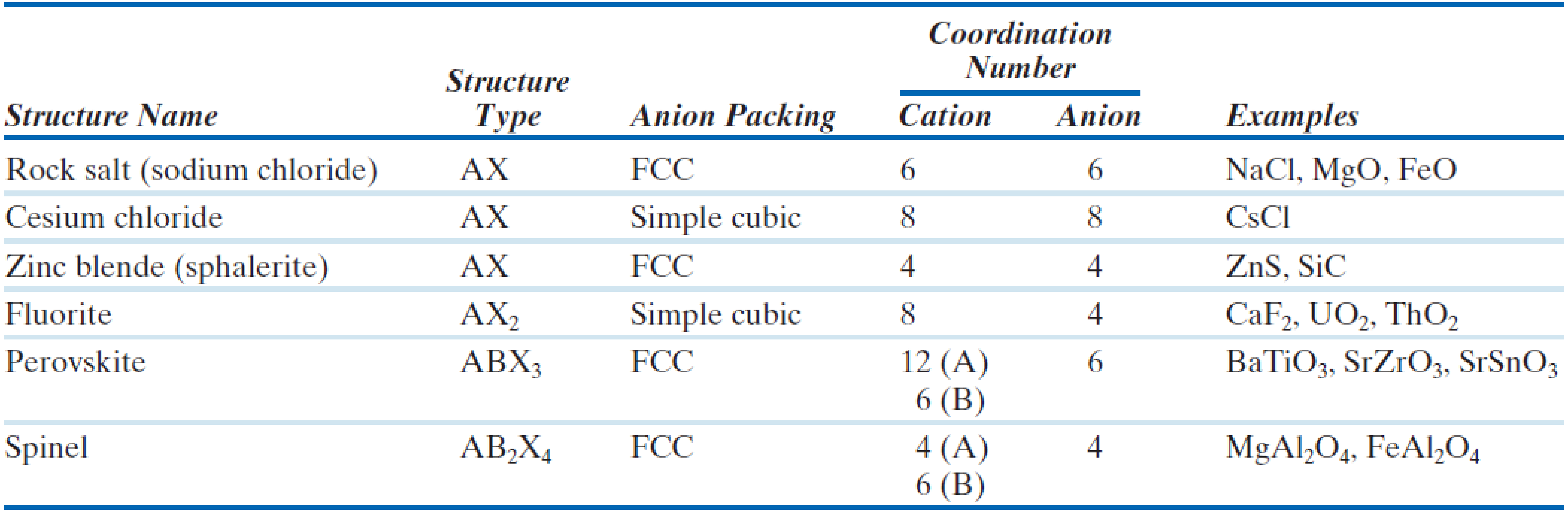


A unit cell for the cesium chloride (CsCl) crystal structure.



A unit cell for the zinc blende (ZnS) crystal structure.

INTRODUCTION



Structure Name	Structure Type	Anion Packing	Coordination Number		Examples
			Cation	Anion	
Rock salt (sodium chloride)	AX	FCC	6	6	NaCl, MgO, FeO
Cesium chloride	AX	Simple cubic	8	8	CsCl
Zinc blende (sphalerite)	AX	FCC	4	4	ZnS, SiC
Fluorite	AX_2	Simple cubic	8	4	CaF_2, UO_2, ThO_2
Perovskite	ABX_3	FCC	12 (A) 6 (B)	6	$BaTiO_3$, $SrZrO_3$, $SrSnO_3$
Spinel	AB_2X_4	FCC	4 (A) 6 (B)	4	$MgAl_2O_4$, $FeAl_2O_4$

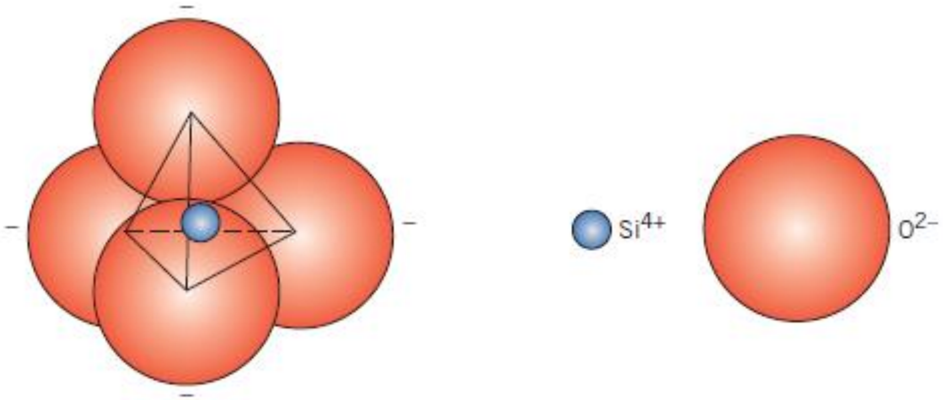
INTRODUCTION

SILICATE CERAMICS

Silicates are materials composed primarily of silicon and oxygen, the two most abundant elements in Earth’s crust; consequently, the bulk of soils, rocks, clays, and sand come under the silicate classification.

Rather than characterizing the crystal structures of these materials in terms of unit cells, it is more convenient to use various arrangements of an SiO4– 4 tetrahedron. Each atom of silicon is bonded to four oxygen atoms, which are situated at the corners of the tetrahedron; the silicon atom is positioned at the center.

Because this is the basic unit of the silicates, it is often treated as a negatively charged entity.



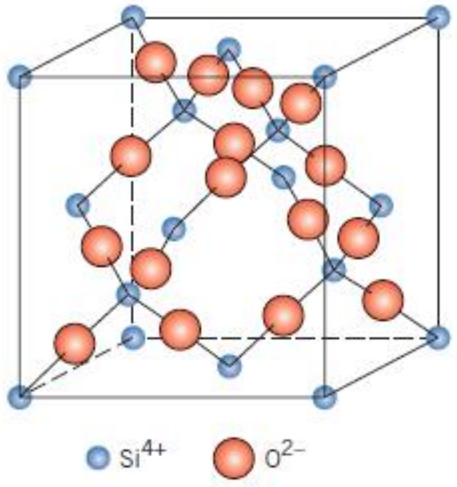
INTRODUCTION

Often the silicates are not considered to be ionic because there is a significant covalent character to the interatomic Si–O bonds, which are directional and relatively strong.

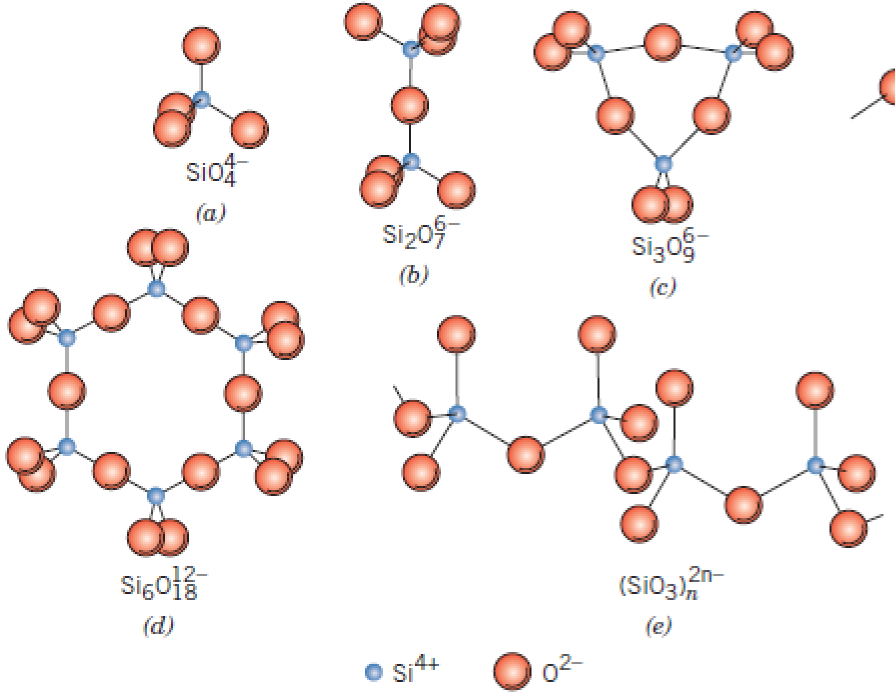
Regardless of the character of the Si–O bond, there is a formal charge of −4 associated with every SiO4− 4 tetrahedron because each of the four oxygen atoms requires an extra electron to achieve a stable electronic structure.

Various silicate structures arise from the different ways in which the SiO4− 4 units can be combined into one-, two-, and three-dimensional arrangements.

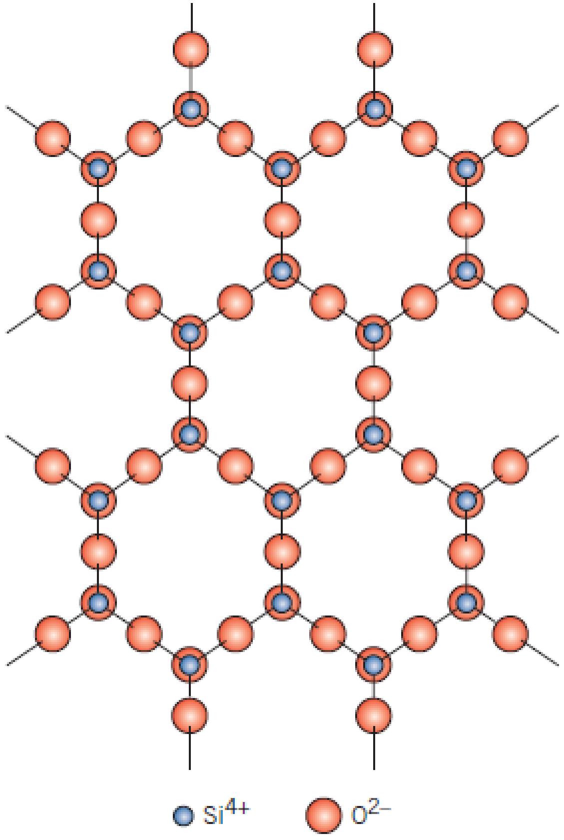
INTRODUCTION



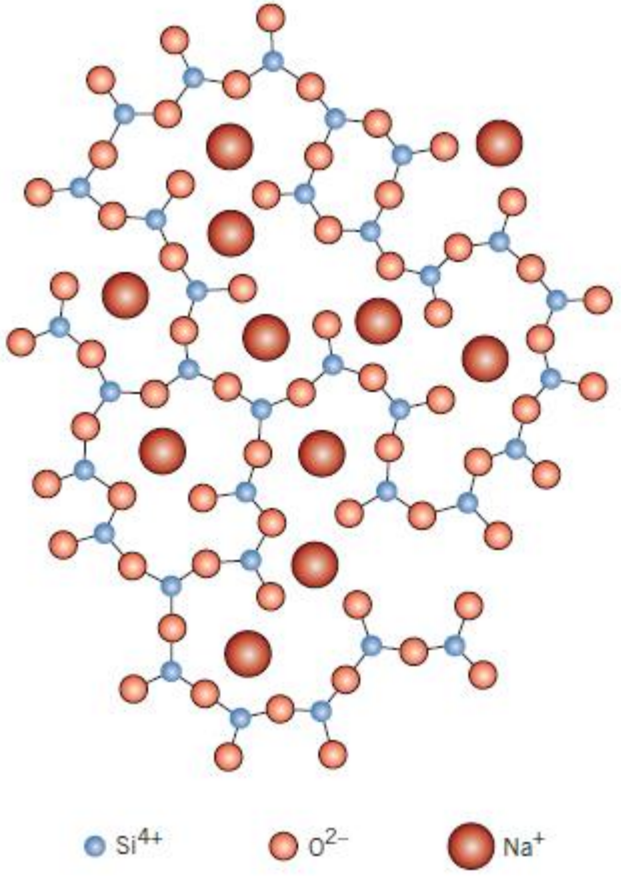
Silica



The Silicates



Layered Silicates



Silica Glasses

INTRODUCTION

CARBON

Although not one of the most frequently occurring elements found on Earth, carbon affects our lives in diverse and interesting ways. It exists in the elemental state in nature, and solid carbon has been used by all civilizations since prehistoric times.

In today’s world, the unique properties (and property combinations) of the several forms of carbon make it extremely important in many commercial sectors, including some cutting-edge technologies.

Carbon exists in two allotropic forms—diamond and graphite—as well as in the amorphous state. The carbon group of materials does not fall within any of the traditional metal, ceramic, or polymer classification schemes.

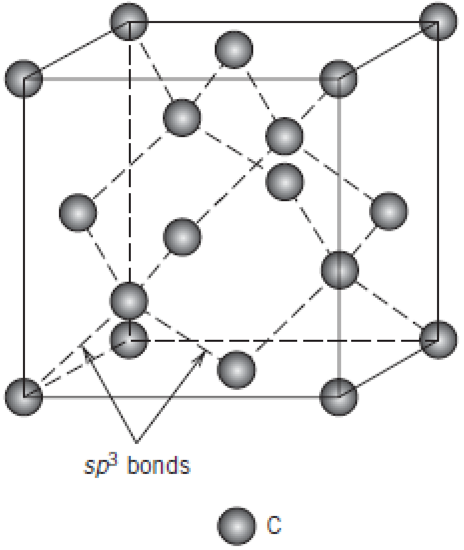
Graphite is sometimes classified as a ceramic. This treatment of the carbons focuses primarily on the structures of diamond and graphite.

INTRODUCTION

Diamond

Diamond is a metastable carbon polymorph at room temperature and atmospheric pressure.
Its crystal structure is a variant of the zinc blende structure in which carbon atoms occupy all positions (both Zn and S); the unit cell for diamond is shown.

Each carbon atom has undergone *sp*3 hybridization so that it bonds (tetrahedrally) to four other carbons; these are extremely strong covalent bonds.



The crystal structure of diamond is appropriately called the *diamond cubic* crystal structure, which is also found for other Group IVA elements in the periodic table [e.g., germanium, silicon, and gray tin below 13°C (55°F)].

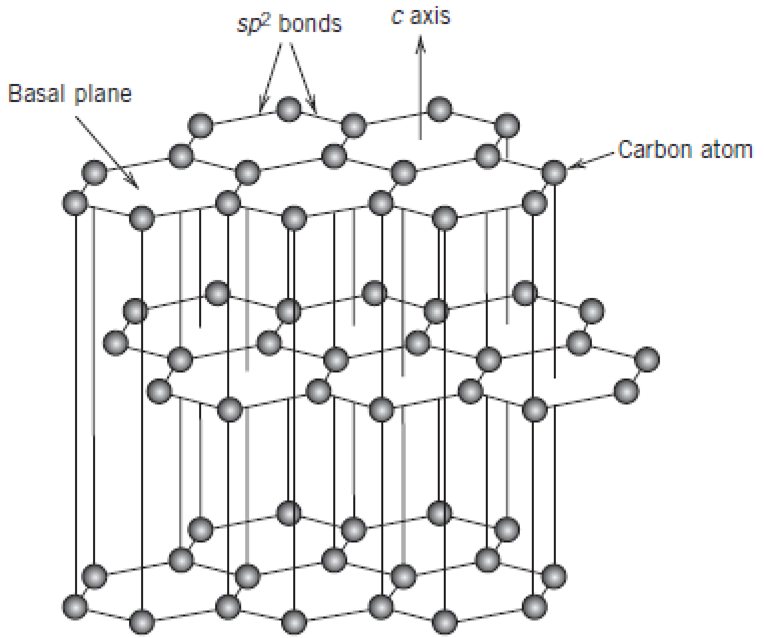
INTRODUCTION

Graphite

Another polymorph of carbon, graphite, has a crystal structure distinctly different from that of diamond; furthermore, it is a stable polymorph at ambient temperature and pressure.

For the graphite structure, carbon atoms are located at corners of interlocking regular hexagons that lie in parallel (basal) planes.

Within these planes (layers or sheets), *sp*2 hybrid orbitals bond each carbon atom to three other adjacent and coplanar carbons atoms; these bonds are strong covalent ones.



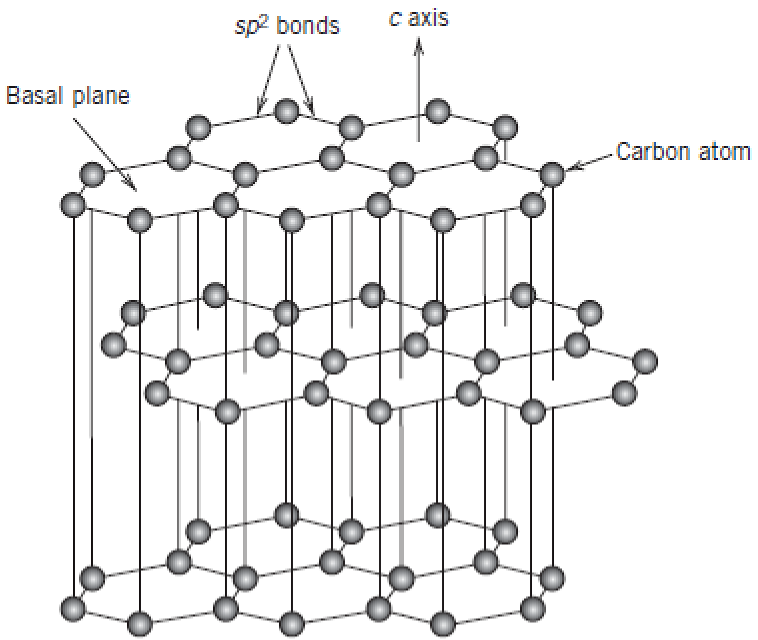
INTRODUCTION

This hexagonal configuration assumed by *sp*2 bonded carbon atoms is represented.

In addition, each atom’s fourth bonding electron is *delocalized* (i.e., does not belong to a specific atom or bond).

Rather, its orbital becomes part of a molecular orbital that extends over adjacent atoms and resides between layers.

Interlayer bonds are directed perpendicular to these planes and are of the weak van der Waals type.



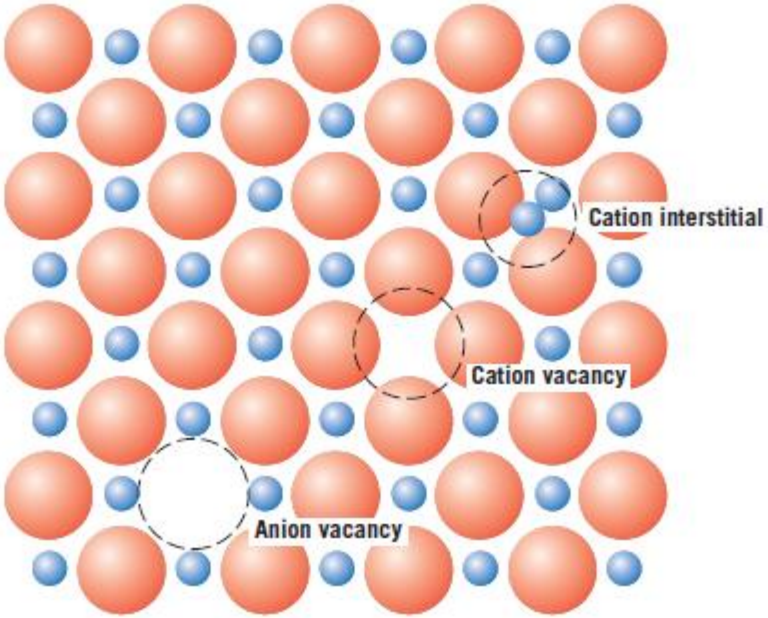
IMPERFECTIONS IN CERAMICS

Atomic Point Defects

Atomic defects involving host atoms may exist in ceramic compounds. As with metals,
both vacancies and interstitials are possible; however, because ceramic materials contain
ions of at least two kinds, defects for each ion type may occur.

For example, in NaCl, Na interstitials and vacancies and Cl interstitials and vacancies may exist. It is highly improbable that there would be appreciable concentrations of anion interstitials.

The anion is relatively large, and to fit into a small interstitial position, substantial strains on the surrounding ions must be introduced.



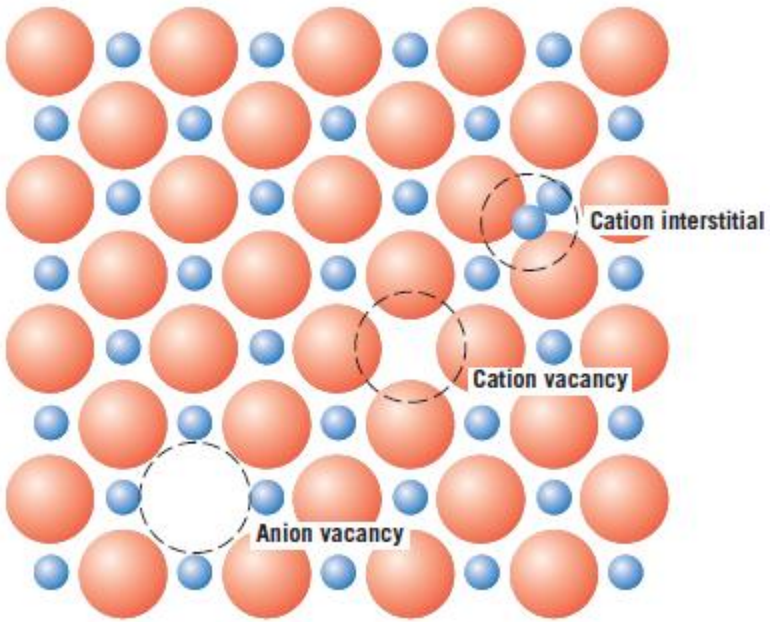
IMPERFECTIONS IN CERAMICS

The expression **defect structure** is often used to designate the types and concentrations of atomic defects in ceramics.

Because the atoms exist as charged ions, when defect structures are considered, conditions of electroneutrality must be maintained.

Electroneutrality is the state that exists when there are equal numbers of positive and negative charges from the ions.

As a consequence, defects in ceramics do not occur alone.

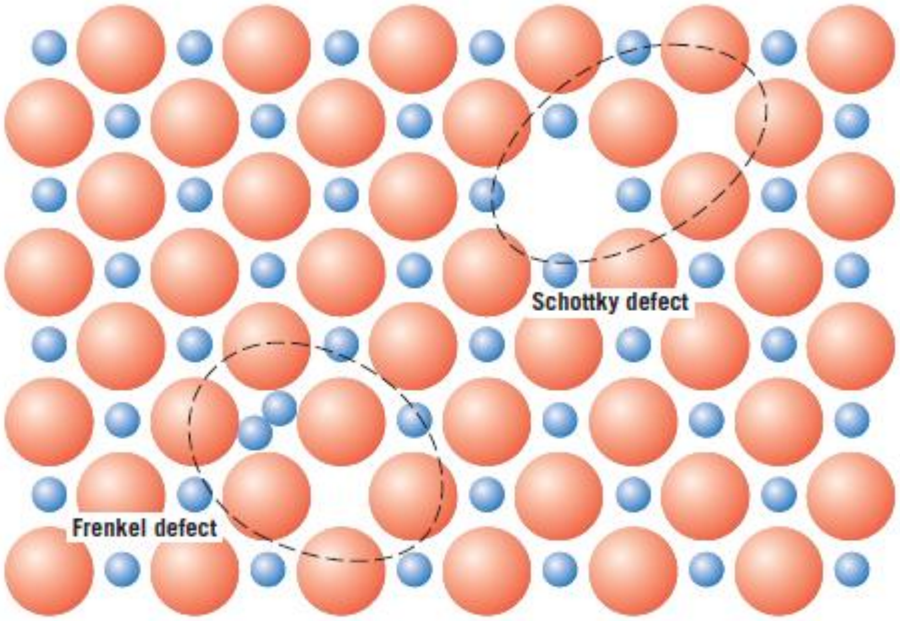


IMPERFECTIONS IN CERAMICS

One such type of defect involves a cation–vacancy and a cation–interstitial pair.

This is called a **Frenkel defect** . It might be thought of as being formed by a cation leaving its normal position and moving into an interstitial site.

There is no change in charge because the cation maintains the same positive charge as an interstitial.

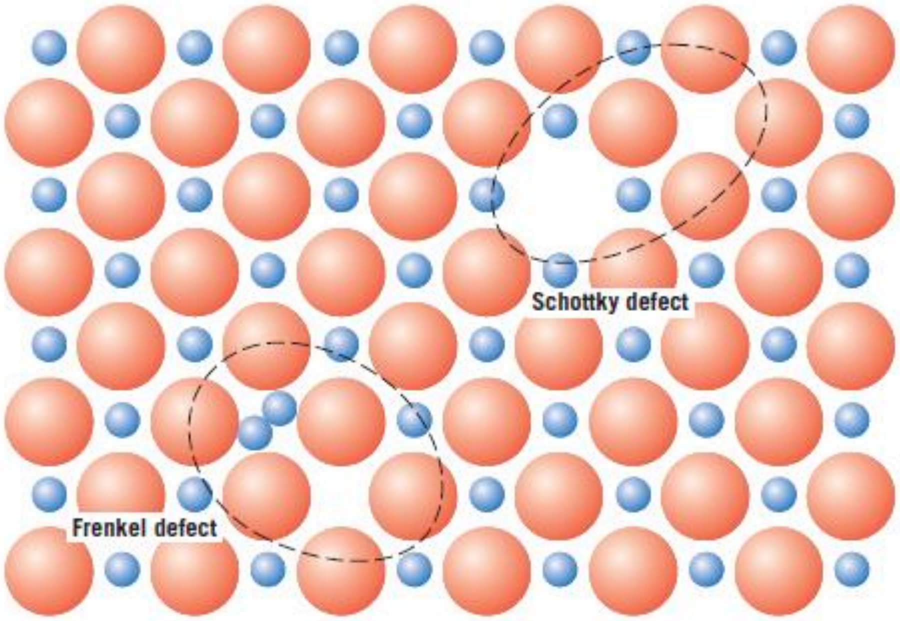


IMPERFECTIONS IN CERAMICS

Another type of defect found in AX materials is a cation vacancy–anion vacancy pair known as a **Schottky defect,** also schematically diagrammed in.

This defect might be thought of as being created by removing one cation and one anion from the interior of the crystal and then placing them both at an external surface.

Because the magnitude of the positive charge on the cation is equal to the magnitude of the negative charge on the anion, and because for every anion vacancy there exists a cation vacancy, the charge neutrality of the crystal is maintained.



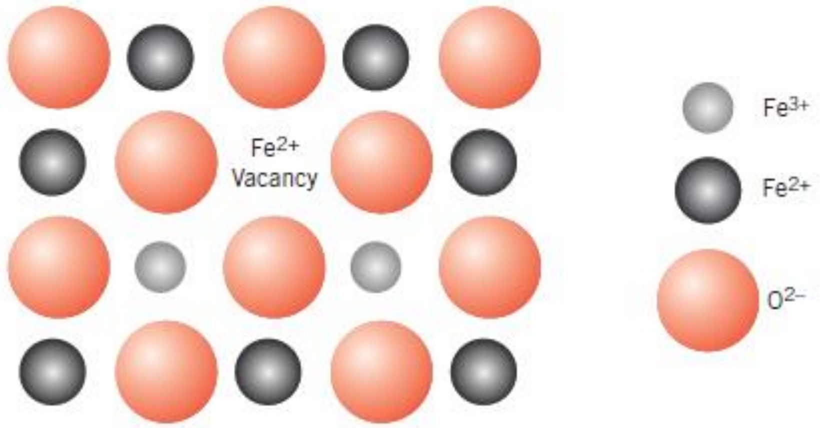
IMPERFECTIONS IN CERAMICS

The ratio of cations to anions is not altered by the formation of either a Frenkel or a Schottky defect.

If no other defects are present, the material is said to be stoichiometric.

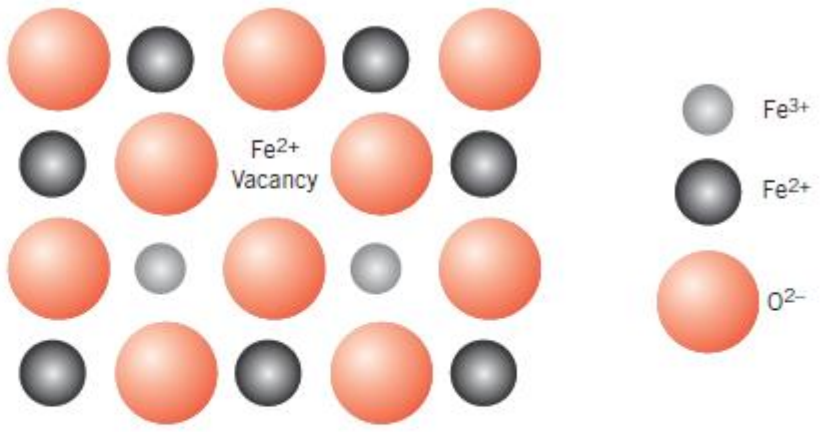
Stoichiometry may be defined as a state for ionic compounds wherein there is the exact ratio of cations to anions as predicted by the chemical formula.

For example, NaCl is stoichiometric if the ratio of Na+ ions to Cl− ions is exactly 1:1. A ceramic compound is *nonstoichiometric* if there is any deviation from this exact ratio.



IMPERFECTIONS IN CERAMICS

Nonstoichiometry may occur for some ceramic materials in which two valence (or ionic) states exist for one of the ion types.



Iron oxide (wüstite, FeO) is one such material because the iron can be present in both Fe2+ and Fe3+ states; the number of each of these ion types depends on temperature and the ambient oxygen pressure.

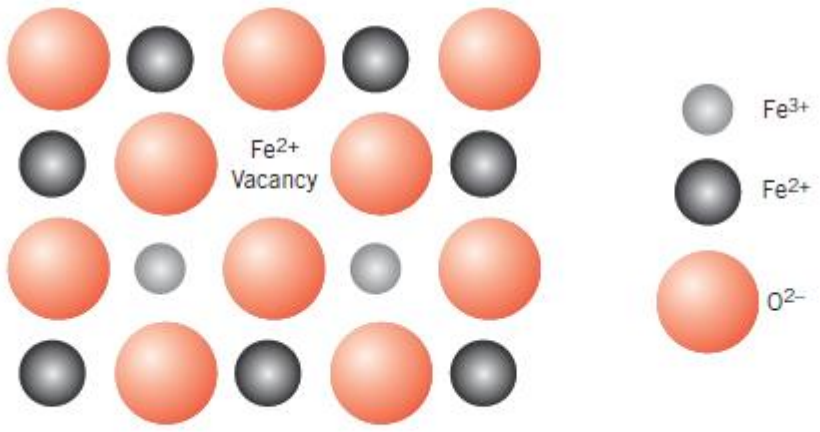
The formation of an Fe3+ ion disrupts the electroneutrality of the crystal by introducing an excess +1 charge, which must be offset by some type of defect.

IMPERFECTIONS IN CERAMICS

This may be accomplished by the formation of one Fe^{2+} vacancy (or the removal of two positive charges) for every two Fe^{3+} ions that are formed.

The crystal is no longer stoichiometric because there is one more O ion than Fe ion; however, the crystal remains electrically neutral.

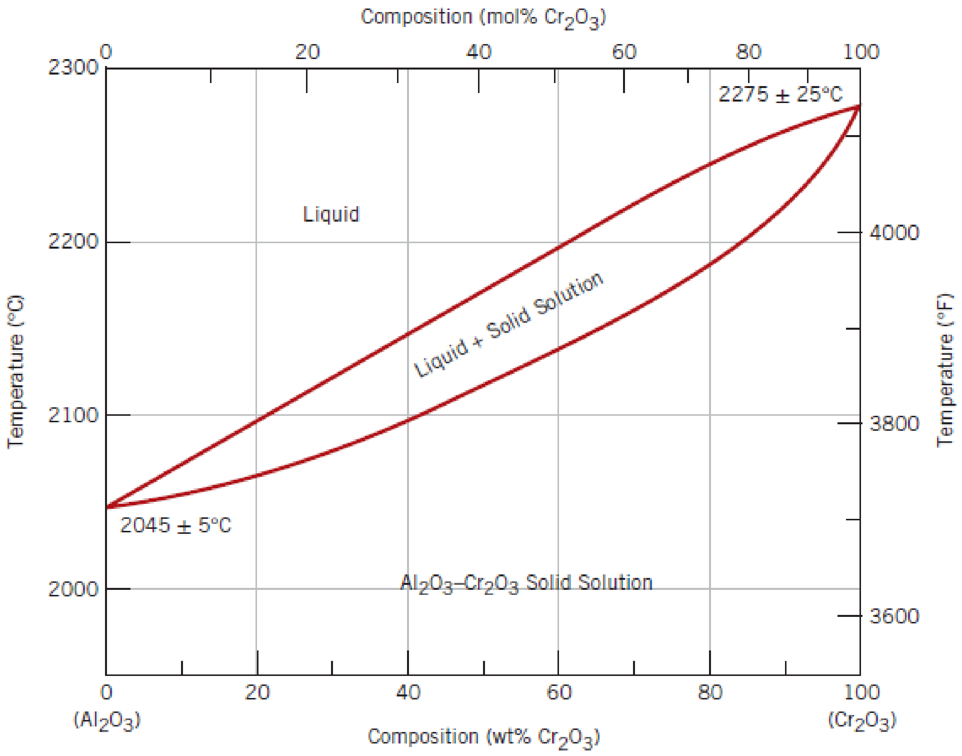
This phenomenon is fairly common in iron oxide, and, in fact, its chemical formula is often written as $Fe_{1-x}O$ (where x is some small and variable fraction substantially less than unity) to indicate a condition of nonstoichiometry with a deficiency of Fe.



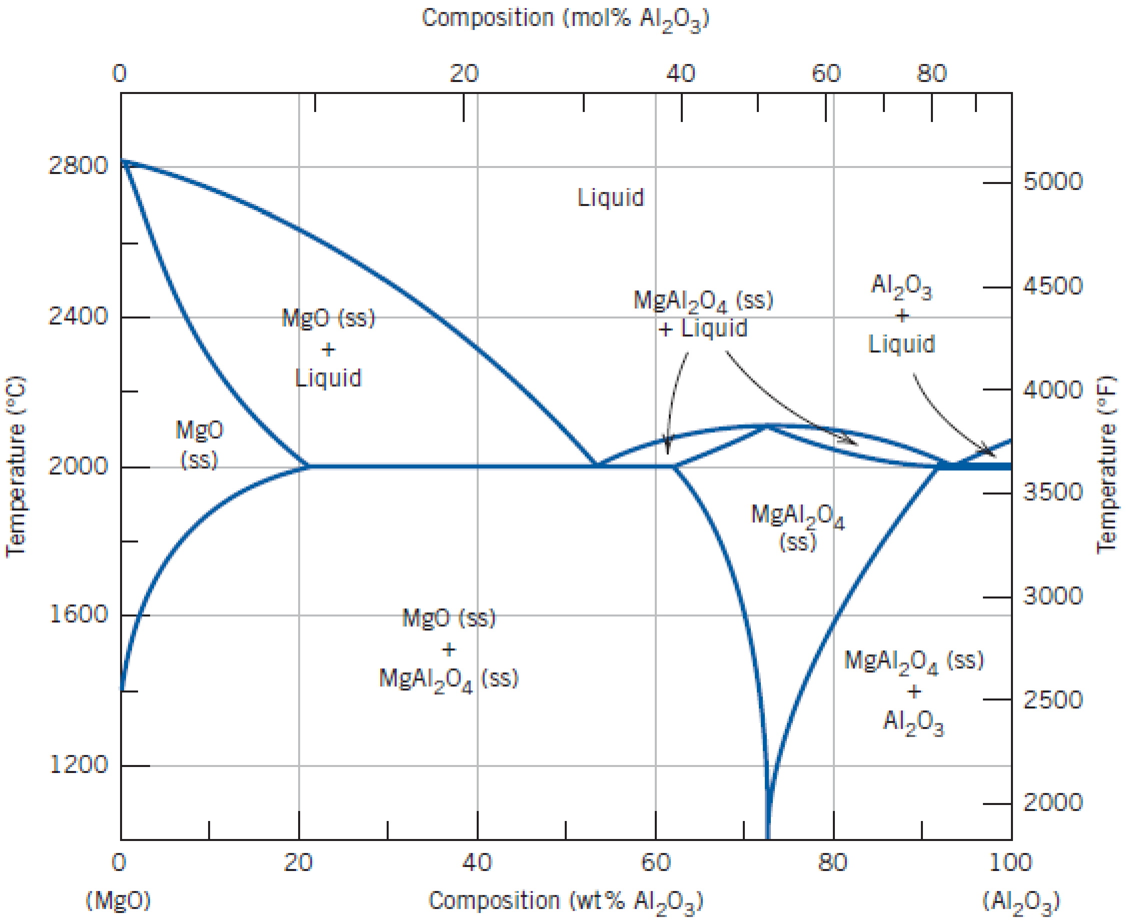
CERAMIC PHASE DIAGRAMS

Phase diagrams have been experimentally determined for many ceramic systems. For binary or two-component phase diagrams, it is frequently the case that the two components are compounds that share a common element, often oxygen.

The aluminum oxide–chromium oxide phase diagram. (Adapted from E. N. Bunting, "Phase Equilibria in the System Cr_2O_3–Al_2O_3," *Bur. Standards J. Research,* 6, 1931, p. 948.)



CERAMIC PHASE DIAGRAMS

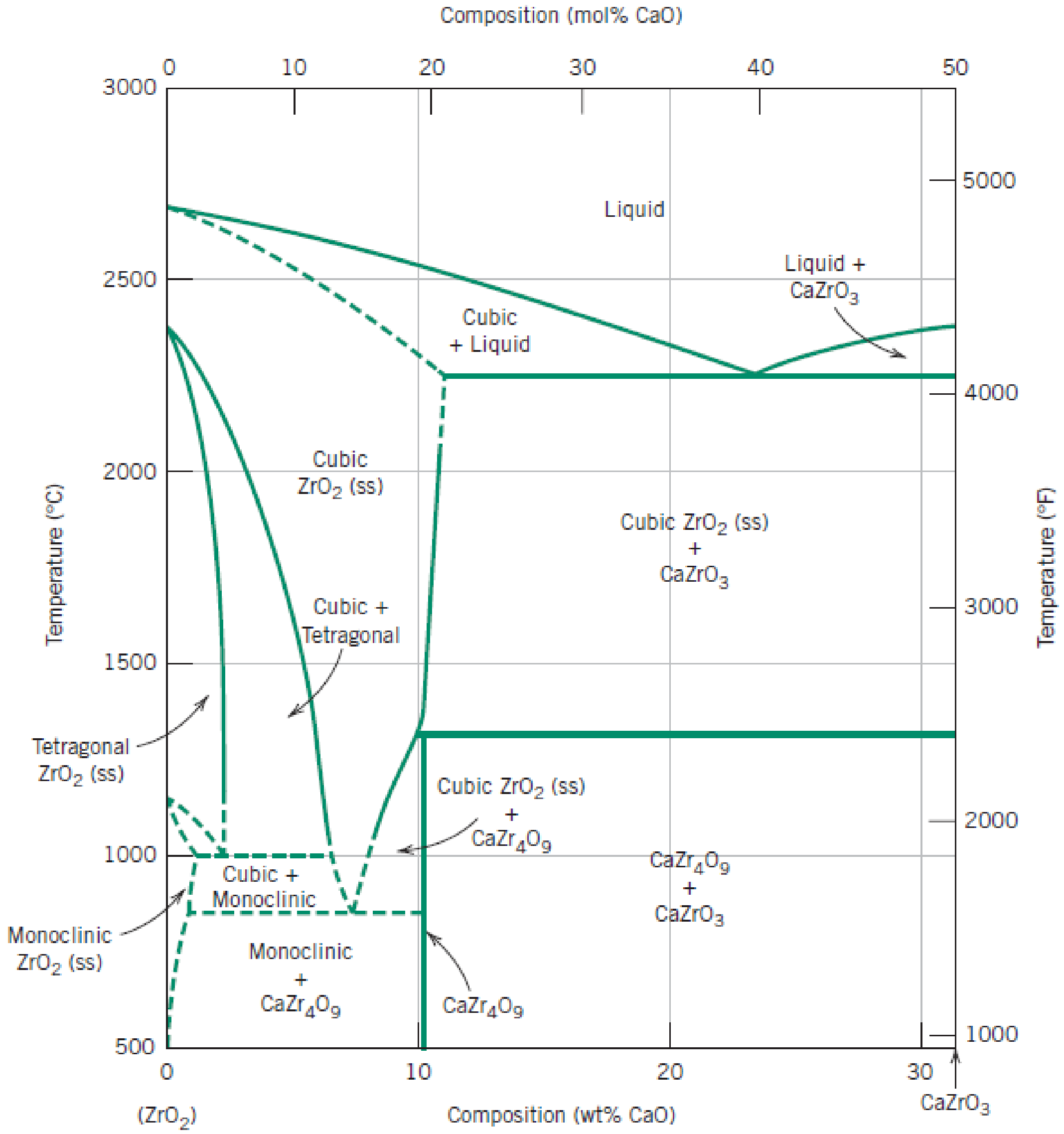


The magnesium oxide–aluminum oxide phase diagram; ss denotes solid solution. (Adapted from B. Hallstedt, "Thermodynamic Assessment of the System $MgO–Al_2O_3$," *J. Am. Ceram. Soc.*, 75[6], 1992, p. 1502. Reprinted by permission of the American Ceramic Society.)

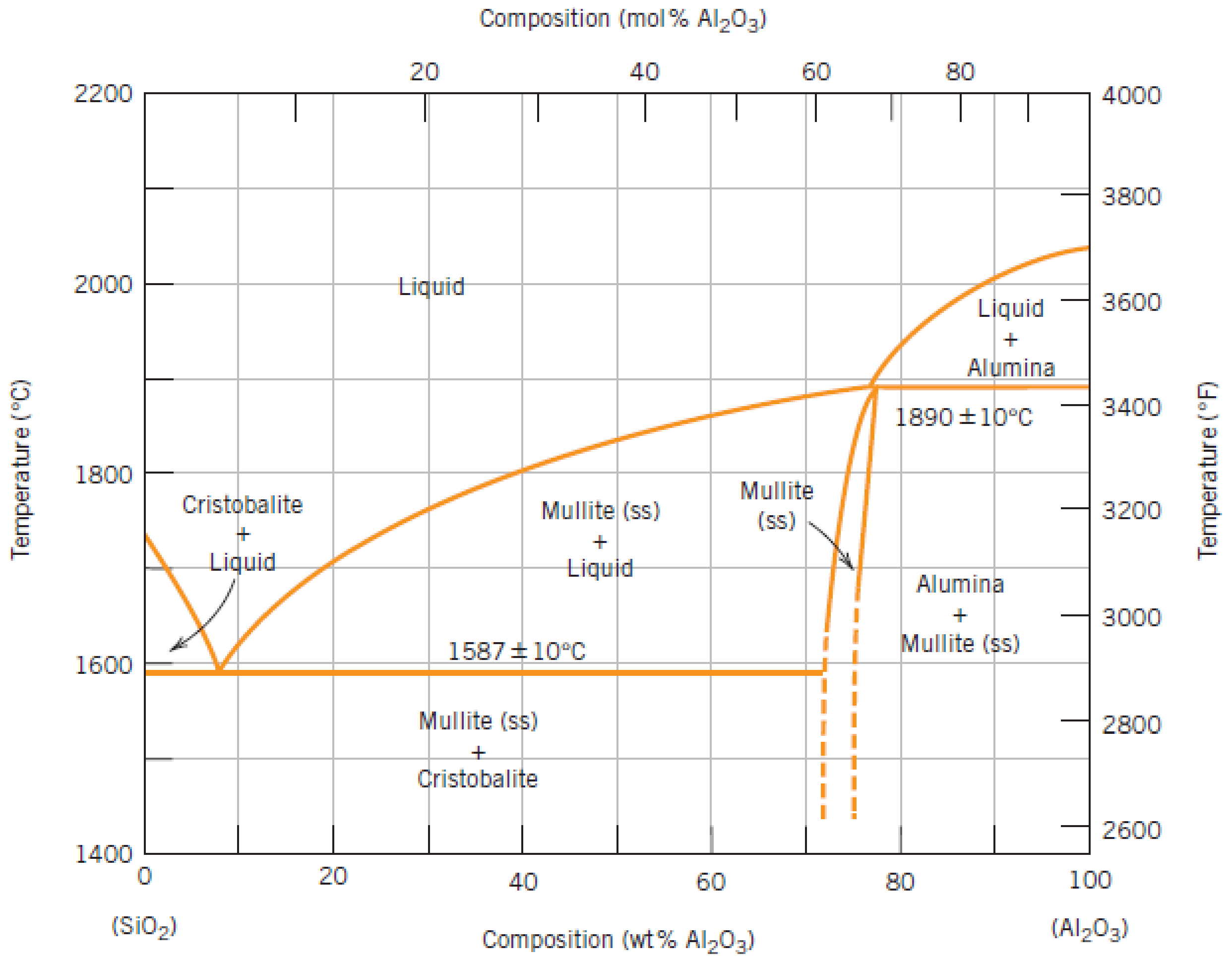
CERAMIC PHASE DIAGRAMS

A portion of the zirconia–calcia phase diagram; ss denotes solid solution.

(Adapted from V. S. Stubican and S. P. Ray, "Phase Equilibria and Ordering in the System ZrO_2–CaO," *J. Am. Ceram. Soc.*, 60[11–12], 1977, p. 535. Reprinted by permission of the American Ceramic Society.)



CERAMIC PHASE DIAGRAMS



The silica–alumina phase diagram; ss denotes solid solution.
(Adapted from F. J. Klug, S. Prochazka, and R. H. Doremus, "Alumina–Silica Phase Diagram in the Mullite Region," *J. Am. Ceram. Soc.*, 70[10], 1987, p. 758. Reprinted by permission of the American Ceramic Society.)

MECHANICAL PROPERTIES

Brittle Fracture of Ceramics

- For ceramic materials, microcracks, the presence of which is very difficult to control, result in amplification of applied tensile stresses and account for relatively low fracture strengths (flexural strengths).
- Considerable variation in fracture strength for specimens of a specific material results inasmuch as the size of a crack initiating flaw varies from specimen to specimen.
- This stress amplification does not occur with compressive loads; consequently, ceramics are stronger in compression.
- Fractographic analysis of the fracture surface of a ceramic material may reveal the location and source of the crack-producing flaw.

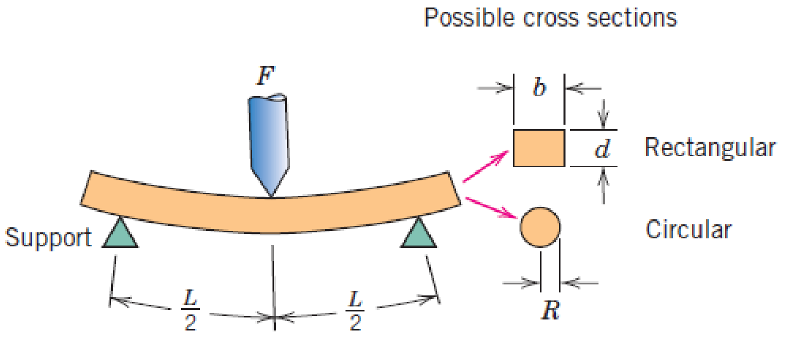
MECHANICAL PROPERTIES

Stress–Strain Behavior

- The stress–strain behaviors and fracture strengths of ceramic materials are determined using transverse bending tests.
- Flexural strengths as measured from three-point transverse bending tests may be determined for rectangular and circular cross-sections using, respectively, Equations:

$$\sigma_{fs} = \frac{3F_f L}{2bd^2}$$

$$\sigma_{fs} = \frac{F_f L}{\pi R^3}$$



σ = stress = $\frac{Mc}{I}$

where M = maximum bending moment
c = distance from center of specimen to outer fibers
I = moment of inertia of cross section
F = applied load

	M	c	I	σ
Rectangular	$\frac{FL}{4}$	$\frac{d}{2}$	$\frac{bd^3}{12}$	$\frac{3FL}{2bd^2}$
Circular	$\frac{FL}{4}$	R	$\frac{\pi R^4}{4}$	$\frac{FL}{\pi R^3}$

MECHANICAL PROPERTIES

Mechanisms of Plastic Deformation

- Any plastic deformation of crystalline ceramics is a result of dislocation motion; the brittleness of these materials is explained, in part, by the limited number of operable slip systems.
- The mode of plastic deformation for noncrystalline materials is by viscous flow; a material's resistance to deformation is expressed as viscosity (in units of Pa·s). At room temperature, the viscosities of many noncrystalline ceramics are extremely high.

Influence of Porosity

- Many ceramic bodies contain residual porosity, which is deleterious to both their moduli of elasticity and fracture strengths.
- Modulus of elasticity depends on and decreases with volume fraction porosity. The diminishment of flexural strength with volume fraction porosity is described by:

$$\sigma_{fs} = \sigma_0 \exp(-nP)$$

MECHANICAL PROPERTIES

Hardness

- Hardness of ceramic materials is difficult to measure because of their brittleness and susceptibility to cracking when indented.

- Micro-indentation Knoop and Vickers techniques are normally used, which employ pyramidal-shaped indenters.

- The hardest known materials are ceramics, which characteristic makes them especially attractive for use as abrasives.