

**Chapter 11, Problem 1**

Define a ceramic material.

**Chapter 11, Solution 1**

Ceramic materials are inorganic, nonmetallic materials that consist of metallic and nonmetallic elements bonded together primarily by ionic and/or covalent bonds.

**Chapter 11, Problem 2**

What are some properties common to most ceramic materials?

**Chapter 11, Solution 2**

While the properties of ceramic materials vary greatly, most ceramic materials are hard and brittle with low toughness and ductility but good electrical and thermal insulating properties. Also, ceramic materials typically have high melting temperatures and high chemical stability.

**Chapter 11, Problem 3**

Distinguish between traditional and engineering ceramic materials and give examples of each.

**Chapter 11, Solution 3**

Traditional ceramic materials are typically made from three components – clay, feldspar and silica – whereas engineering ceramics consist of pure or nearly pure compounds such as aluminum oxide ( $\text{Al}_2\text{O}_3$ ), silicon carbide (SiC), and silicon nitride ( $\text{Si}_3\text{N}_4$ ). Examples of traditional ceramics include bricks, tiles and electrical porcelain while applications of engineering ceramics include silicon carbide parts for high temperature gas turbine engine components, zirconium dioxide crucibles for melting superalloys, and high performance ball bearing and races made of titanium and carbon nitride.

**Chapter 11, Problem 4**

What two main factors affect the packing of ions in ionic solids?

**Chapter 11, Solution 4**

The two main factors which affect the packing of ions in ionic solids are:

1. The relative size of the ions in the ionic solid, assuming the ions are hard spheres with definite radii;
2. The need to balance the electrostatic charges to maintain electrical neutrality within the ionic solid.

**Chapter 11, Problem 5**

Define (a) coordination number and (b) critical radius ratio for the packing of ions in ionic solids.

**Chapter 11, Solution 5**

(a) The coordination number is the number of anions that surround a central cation.

(b) The critical radius ratio is the ratio of the radius of the central cation to the radius of the surrounding anions.

**Chapter 11, Problem 6**

What is the spinel crystal structure?

**Chapter 11, Solution 6**

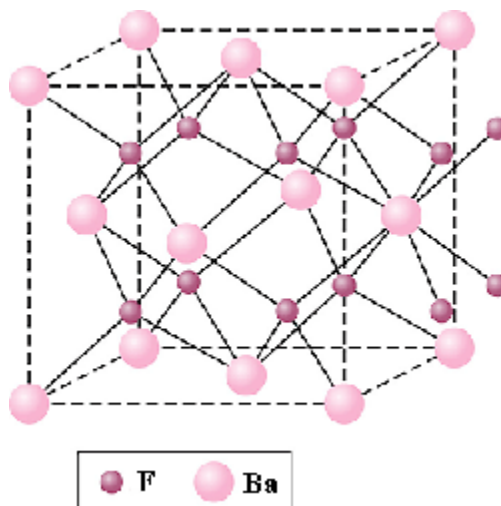
The spinel structure has the general form  $AB_2O_4$  where A represents a metal ion with a +2 valence and B is a metal cation with a +3 valence. The oxygen ions form an FCC lattice in which the A and B ions occupy the octahedral and tetrahedral interstitial sites.

**Chapter 11, Problem 7**

Draw the unit cell for  $BaF_2$ , which has the fluorite ( $CaF_2$ ) crystal structure. If the  $Ba^{2+}$  ions occupy the FCC lattice sites, which sites do the  $F^-$  ions occupy?

**Chapter 11, Solution 7**

The  $BaF_2$  unit cell is shown below. With the  $Ba^{2+}$  ions occupying the FCC lattice sites, the  $F^-$  ions occupy the tetrahedral interstitial sites.



### Chapter 11, Problem 8

What fraction of the octahedral interstitial sites are occupied in the  $\text{CaF}_2$  structure?

### Chapter 11, Solution 8

All eight of the tetrahedral interstitial sites are occupied. However, none of the four octahedral interstitial sites are occupied; thus the fraction is **zero**.

### Chapter 11, Problem 9

What is the antifluorite structure? What ionic compounds have this structure? What fraction of the tetrahedral interstitial sites are occupied by cations?

### Chapter 11, Solution 9

The antifluorite structure consists of an FCC unit cell with anions occupying the FCC lattice points and cations occupying all eight tetrahedral sites. Thus the cation and anion positions of the fluorite structure are reversed. Examples of compounds having this structure are  $\text{Li}_2\text{O}$ ,  $\text{Na}_2\text{O}$ ,  $\text{K}_2\text{O}$ , and  $\text{Mg}_2\text{O}$ . The fraction of the tetrahedral sites occupied by cations is one (1.0).

### Chapter 11, Problem 10

Describe the perovskite structure. What fraction of the octahedral interstitial sites are occupied by the tetravalent cation?

### Chapter 11, Solution 10

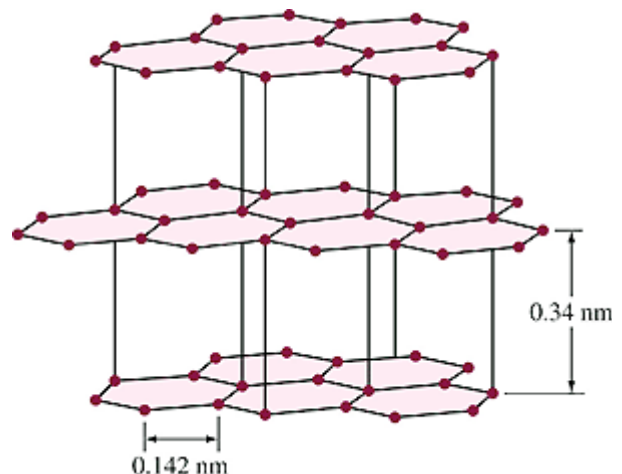
The perovskite structure ( $\text{CaTiO}_3$ ) consists of an FCC unit cell with  $\text{Ca}^{2+}$  cations in the corners,  $\text{O}^{2-}$  anions in the face centers, and a  $\text{Ti}^{4+}$  cation in the center octahedral interstitial site. The tetravalent cation  $\text{Ti}^{4+}$  fills one-fourth of the octahedral sites.

### Chapter 11, Problem 11

Draw a section of the graphite structure. Why are the layers of graphite able to slide past each other easily?

### Chapter 11, Solution 11

The layers of graphite within the graphite structure can easily slide past each other because the bonds between the layers are weak secondary bonds, as compared to the strong covalent bonds between the carbon atoms constituting the layers.



**Chapter 11, Problem 12**

Describe and illustrate the following silicate structures: (a) island, (b) chain, and (c) sheet.

**Chapter 11, Solution 12**

- (a) Island silicate structures are formed when positive ions, such as  $\text{Mg}^{2+}$  and  $\text{Fe}^{2+}$  bond with oxygen anions of the  $\text{SiO}_4^{4-}$  tetrahedra.
- (b) Chain or ring structures are produced when two corners of each  $\text{SiO}_4^{4-}$  tetrahedron bond with the corners of two other tetrahedra. The result is the  $\text{SiO}_3^{2-}$  structure.
- (c) Sheet silicate structures form when three corners in the same plane of a silicate tetrahedron are bonded to the corners of three other silicate tetrahedra. The unit chemical formula of this structure is  $\text{Si}_2\text{O}_5^{2-}$ .

**Chapter 11, Problem 13**

Describe the structure of a sheet of kaolinite.

**Chapter 11, Solution 13**

A sheet of kaolinite consists of a negatively charged silicate sheet ( $\text{Si}_2\text{O}_5^{2-}$ ) bonded to a positively charged sheet of  $\text{Al}_2(\text{OH})_4^{2+}$ . This composite sheet is comprised of small, flat hexagonal plates of parallel sheets bonded by weak secondary bonds.

**Chapter 11, Problem 14**

Describe the bonding arrangement in the cristobalite (silica) network structure.

**Chapter 11, Solution 14**

In the cristobalite silica structure, each silicon atom is bonded to four oxygen atoms and each oxygen atom forms part of two  $\text{SiO}_4^{4-}$  tetrahedra. The resulting network structure is a common crystalline phase of silica which exists at high temperatures of 1470 to 1710°C.

**Chapter 11, Problem 15**

Describe the feldspar network structure.

**Chapter 11, Solution 15**

In the feldspar silicate structural network, some of the  $\text{Si}^{4+}$  ions are replaced by  $\text{Al}^{3+}$  ions. The resulting negatively charged network is balanced by large cations of the alkali and alkaline earth elements, such as  $\text{Na}^+$ ,  $\text{K}^+$ , and  $\text{Ca}^{2+}$ , which fit into the interstitial sites.

**Chapter 11, Problem 16**

What are the basic steps in the processing of ceramic products by the agglomeration of particles?

**Chapter 11, Solution 16**

The basic steps in the processing of ceramic products by the agglomeration are:

1. material preparation
2. forming or casting
3. thermal treatment by drying and firing to a high enough temperature for the particles to bond.

**Chapter 11, Problem 17**

What types of ingredients are added to ceramic particles in preparing ceramic raw materials for processing?

**Chapter 11, Solution 17**

Binders, lubricants and other additives are added to ceramic particles to achieve the desired set of ceramic properties.

**Chapter 11, Problem 18**

Describe two methods for preparing ceramic raw materials for processing.

**Chapter 11, Solution 18**

Ceramic raw materials are prepared by wet processing, dry processing or a combination of wet and dry processing. In wet processing, the additives are blended with water while in dry processing, the additives are ground dry with the raw materials.

**Chapter 11, Problem 19**

Describe the dry-pressing method for producing such ceramic products as technical ceramic compounds and structural refractories. What are the advantages of dry-pressing ceramic materials?

**Chapter 11, Solution 19**

In dry pressing, granular ceramic powder, in solution with small amounts of water and/or organic binder, is simultaneously compacted and shaped in a die. Subsequently, the parts are typically fired to achieve the desired microstructural properties such as strength. The advantages of dry-pressing ceramic materials are the ability to rapidly form a wide variety of shapes and the capability to achieve uniformity and close tolerances.

**Chapter 11, Problem 20**

Describe the isostatic-pressing method for producing ceramic products.

**Chapter 11, Solution 20**

In the isostatic process, the ceramic powder is loaded into a flexible airtight container that is inside a chamber of hydraulic fluid. Pressure is then applied to the fluid to compact the powder uniformly. The product, which possesses the shape of the container, is fired to attain the required microstructure and properties.

**Chapter 11, Problem 21**

Describe the four stages in the manufacture of a spark of plug insulator.

**Chapter 11, Solution 21**

In manufacturing a spark plug insulator, four stages are completed: isostatic pressing, turning the blank, firing to fuse the powder, and glazing.

**Chapter 11, Problem 22**

What are the advantages of hot-pressing ceramics materials?

**Chapter 11, Solution 22**

The advantages of hot-pressing ceramics materials are producing improved mechanical properties and achieving high densities.

**Chapter 11, Problem 23**

Describe the steps in the slip-casting process for ceramic products.

### **Chapter 11, Solution 23**

In the slip-casting process, five steps must be completed:

1. A powdered ceramic material and a liquid are prepared as a stable suspension called a slip.
2. The slip is poured into a porous mold which absorbs some of the slip liquid. The remaining slip forms a semihard layer on the mold surface.
3. For a drain casting process, excess slip is poured out of the cavity once a sufficient wall thickness has formed. For a solid casting process, casting is continued until the entire mold cavity is filled.
4. The material in the mold is allowed to dry to provide adequate strength for handling and the subsequent removal of the part from the mold.
5. Finally, the cast part is fired to attain the required microstructure and properties.

### **Chapter 11, Problem 24**

What is the difference between (a) drain and (b) solid slip casting?

### **Chapter 11, Solution 24**

Refer to step (3) in the solution to Problem 11.41.

### **Chapter 11, Problem 25**

What are the advantages of slip casting?

### **Chapter 11, Solution 25**

Advantages of slip casting include the ability to form parts with thin-walls and complex shapes and the low cost associated with creating developmental parts and short production runs.

### **Chapter 11, Problem 26**

What types of ceramic products are produced by extrusion? What are the advantages of this process? Limitations?

### **Chapter 11, Solution 26**

Extrusion is used to produce ceramic products which have a uniform cross-section (bricks and tiles) and which are hollow (sewer pipes). The advantages associated with this process include the ability to efficiently form a single long shape which is subsequently cut to the desired lengths and the ability to achieve close tolerances. However, the extrusion process is limited by the need to produce a constant cross-section and by the need to cool the extruded part by air-blast or water cooling.

**Chapter 11, Problem 27**

What are the purposes of drying ceramic products before firing?

**Chapter 11, Solution 27**

Ceramics are dried before firing in order to remove water and organic binders.

**Chapter 11, Problem 28**

What is the sintering process? What occurs to the ceramic particles during sintering?

**Chapter 11, Solution 28**

The sintering process is a thermal treatment which causes ceramic particles to bond together by solid-state diffusion. This diffusion process, driven by high temperatures, occurs between the contacting surfaces of the particles and allows them to chemically bond. As the process proceeds, the sintered particles increase in size until an equilibrium grain size is attained. The energy of the surfaces of these grain boundaries is lower than the surface energy associated with the original individual particles.

**Chapter 11, Problem 29**

What is the vitrification process? In what type of ceramic materials does vitrification take place?

**Chapter 11, Solution 29**

In the vitrification process, the glass phase of the ceramic liquefies and fills the material's pores during firing, and then solidifies during cooling to form a vitreous or glassy matrix that bonds the particles. This process takes place in ceramic materials containing a glass phase such as porcelain and structural clay.

**Chapter 11, Problem 30**

What are the three basic components of traditional ceramics?

**Chapter 11, Solution 30**

The three basic components of traditional ceramics are clay, silica (flint) and feldspar.

**Chapter 11, Problem 31**

What is the approximate composition of kaolin clay?

**Chapter 11, Solution 31**

The approximate composition of kaolin clay is 45.5 percent  $\text{SiO}_2$ , 37.4 percent  $\text{Al}_2\text{O}_3$ , 13.9 percent  $\text{H}_2\text{O}$ , 1.68 percent  $\text{Fe}_2\text{O}_3$ , 1.30 percent  $\text{TiO}_2$ , 0.03 percent  $\text{MgO}$ , 0.011 percent  $\text{Na}_2\text{O}$ , 0.004 percent  $\text{CaO}$ , and 0.005 percent  $\text{K}_2\text{O}$ .



**Chapter 11, Problem 32**

What is the role of clay in traditional ceramics?

**Chapter 11, Solution 32**

In traditional ceramics, clay constitutes the primary component of the ceramic and makes the material workable prior to firing.

**Chapter 11, Problem 33**

What is flint? What role does it have in traditional ceramics?

**Chapter 11, Solution 33**

Flint, also called quartz, is silica ( $\text{SiO}_2$ ) and serves as the refractory component of traditional ceramics.

**Chapter 11, Problem 34**

What is feldspar? What role does it have in traditional ceramics?

**Chapter 11, Solution 34**

Feldspar is an aluminum silicate crystalline mineral containing potassium, sodium or calcium. Because feldspar turns into glass upon firing, it is often used in traditional ceramics to bond together the refractory components.

**Chapter 11, Problem 35**

List some examples of whiteware ceramic products.

**Chapter 11, Solution 35**

Examples of whiteware ceramic products are bone china, dental porcelain, electrical insulation ware, vitreous tile and vitreous sanitary ware.

**Chapter 11, Problem 36**

Why is the term *triaxial* used to describe some whitewares?

**Chapter 11, Solution 36**

The term triaxial refers to the fact that the whiteware is composed of three primary materials – clay, feldspar and flint.

**Chapter 11, Problem 37**

What are the two most important industrial abrasives?

**Chapter 11, Solution 37**

The two most important industrial abrasives are fused alumina ( $\text{Al}_2\text{O}_3$ ) and silicon carbide (SiC).

**Chapter 11, Problem 38**

What are important properties for industrial abrasives?

**Chapter 11, Solution 38**

Properties important to industrial abrasives include: porosity sufficient to allow air or liquid lubricant flow during grinding, cutting and polishing processes; good heat stability for withstanding high frictional heat generation; and high hardness for grinding and cutting processes.

**Chapter 11, Problem 39**

Why do most ceramic materials have low thermal conductivities?

**Chapter 11, Solution 39**

Most ceramic materials have low thermal conductivities because of their strong ionic-covalent bonding which restricts the motion of electrons required for both thermal and electrical conduction. Pure metals are excellent electron carriers and thus serve as important conductors of heat and electricity.

**Chapter 11, Problem 40**

What are refractories? What are some of their applications?

**Chapter 11, Solution 40**

Refractories are materials that have good heat resistance. They are used extensively by the metals, chemical, ceramic and glass industries for applications such as linings for various types of furnaces, kilns, ovens, incinerators and reactors.

**Chapter 11, Problem 41**

What are the two main types of ceramic refractory materials?

**Chapter 11, Solution 41**

The two main types of ceramic refractory materials are acidic refractories and basic refractories.

**Chapter 11, Problem 42**

Give the composition and several applications for the following refractories: (a) silica, (b) fireclay, and (c) high-alumina.

**Chapter 11, Solution 42**

- (a) Silica refractories contain 95 to 99 percent  $\text{SiO}_2$  and are used for chemical reactor linings, glass tank parts, ceramic kilns and coke ovens.
- (b) Fireclays are mixtures of plastic fireclay, flint (silica) clay, and clay grog which give a combined composition of approximately 51 to 54 percent  $\text{SiO}_2$  and 37 to 42 percent  $\text{Al}_2\text{O}_3$ . Their refractory applications include linings for cement, rotary, and lime kilns, linings for aluminum-melting and blast furnaces, and linings for incinerators.
- (c) High-alumina refractories are composed of 45 to 99<sup>+</sup> percent  $\text{Al}_2\text{O}_3$  and 0 to 50 percent  $\text{SiO}_2$ . These materials are used in boiler, phosphate, carbon black and spent-acid furnaces, coke kilns, glass-tank refiner walls, continuous-casting tundish linings, and coal gasification reactor linings.

**Chapter 11, Problem 43**

What do most basic refractories consist of? What are some important properties of basic refractories? What is a main application for these materials?

**Chapter 11, Solution 43**

Most basic refractories consist of magnesia ( $\text{MgO}$ ), lime ( $\text{CaO}$ ), and chrome ore ( $\text{Cr}_2\text{O}_3$ ). Some of the important properties associated with these materials are high bulk densities, high melting temperatures, and good resistance to chemical corrosion by basic slags and oxides. Consequently, these refractories are used mainly for the linings of basic-oxygen steelmaking furnaces.

**Chapter 11, Problem 44**

What is the high-temperature reusable-surface insulation that can withstand temperatures as high as 1260°C made of?

**Chapter 11, Solution 44**

High-temperature reusable surface insulation (HRSI) is made of a silica-fiber compound and can withstand 1260°C (2300°F).

**Chapter 11, Problem 45**

Define a glass.

**Chapter 11, Solution 45**

While glass is a ceramic material – made from inorganic materials at high temperatures– it differs from other ceramics in that its constituents are heated to fusion and then cooled in the rigid state without

crystallization. Thus glass is formally defined as *an organic product of fusion that has cooled to a rigid condition without crystallization.*

**Chapter 11, Problem 46**

What are some of the properties of glasses that make them indispensable for many engineering designs?

**Chapter 11, Solution 46**

Glasses are indispensable to many engineering designs because they possess a unique combination of special properties – transparency, hardness and sufficient strength at room temperature, and excellent corrosion resistance to most environments.

**Chapter 11, Problem 47**

How is a glass distinguished from other ceramic materials?

**Chapter 11, Solution 47**

Unlike all other ceramic materials, glass constituents are heated to fusion and then cooled in the rigid state without crystallization. As a consequence, glass has an amorphous structure rather than crystalline.

**Chapter 11, Problem 48**

Define the glass transition temperature.

**Chapter 11, Solution 48**

The glass transition temperature,  $T_g$ , is the temperature at which the two slopes of a glass specific volume versus temperature curve intersect. Physically, this temperature falls within the narrow temperature range in which a glass changes from a rubbery, soft plastic state to a rigid, brittle glassy state. Thus, the  $T_g$  represents the point at which the material behaves more like a solid than a liquid.

**Chapter 11, Problem 49**

Name two glass-forming oxides. What are their fundamental subunits and their shape?

**Chapter 11, Solution 49**

Silica ( $\text{SiO}_2$ ) and boron oxide ( $\text{B}_2\text{O}_3$ ) are two glass-forming oxides. Their fundamental subunits are respectively, the  $\text{SiO}_4^{4-}$  tetrahedron and the  $\text{BO}_3^{3-}$  flat triangle.

**Chapter 11, Problem 50**

What is fused silica glass? What are some of its advantages and disadvantages?

**Chapter 11, Solution 50**

Fused silica glass is composed of 99.5 percent  $\text{SiO}_2$  and is the most important single-component glass. Its advantageous properties include a high spectral transmission and the ability to withstand radiation without browning. However, it is expensive and difficult to melt and fabricate.

**Chapter 11, Problem 51**

What is the basic composition of soda-lime glass? What are some of its advantages and disadvantages? What are some applications for soda-lime glass?

**Chapter 11, Solution 51**

Soda-lime glass has a basic composition of 71 to 73 percent  $\text{SiO}_2$ , 12 to 14 percent  $\text{Na}_2\text{O}$ , and 10 to 12 percent  $\text{CaO}$ . Advantages of soda-lime glass are its low cost and ease of forming due to a low softening point. Disadvantages include low heat resistance and chemical durability. Some of its applications are windows, containers, electric bulbs, and pressed and blown ware.

**Chapter 11, Problem 52**

Define the following viscosity reference points for glasses: working, softening, annealing, and strain.

**Chapter 11, Solution 52**

The *working point* is the temperature which corresponds to a viscosity of  $10^4$  poises and which represents the thermal state at which glass fabrication operations can be performed.

The *softening point* is the temperature which corresponds to a viscosity of  $10^8$  poises and which represents the thermal state at which glass will flow at an appreciable rate under its own weight.

The *annealing point* is the temperature which corresponds to a viscosity of  $10^{13}$  poises and which represents the thermal state at which internal stresses can be relieved.

The *strain point* is the temperature which corresponds to a viscosity of  $10^{14.5}$  poises and which represents the thermal state below which the glass is rigid and stress relaxation only occurs at a slow rate.

**Chapter 11, Problem 53**

Describe the float-glass process for the production of flat-glass products. What is its major advantage?

**Chapter 11, Solution 53**

In the float-glass process, a ribbon of glass flows out of a melting furnace and into a molten tin bath on which it floats. As the ribbon moves across the bath, it cools under a chemically controlled atmosphere to prevent oxidation. Once the glass surfaces are sufficiently hard, the sheet is removed from the float chamber and passed through a lehr annealing furnace which removes residual stresses. The major advantage of this process over its predecessor, the rolling process, is that a very flat sheet of glass is produced which does not require costly grinding or polishing.

**Chapter 11, Problem 54**

What is tempered glass? How is it produced? Why is tempered glass considerably stronger in tension than annealed glass? What are some applications for tempered glass?

**Chapter 11, Solution 54**

Tempered glass is a high strength glass due to the compressive stresses developed on its surface during “tempering”. It is produced by heating the glass close to its softening temperature and then rapidly cooling the glass surface with air. Because the surfaces are rigid during the cooling of the glass interior, tensile stresses are developed in the interior while compressive stresses form at the surface. Tempered glass is stronger in tension than annealed glass because with tempered glass, the applied tensile stress must surpass the surface compressive stress before causing fracture. This glass is used in applications where safety is paramount, such as automobile windows and safety glass doors.

**Chapter 11, Problem 55**

What is chemically strengthened glass? Why is chemically strengthened glass stronger in tension than annealed glass?

**Chapter 11, Solution 55**

Chemically strengthened glass is a glass that has been given a chemical treatment to introduce large ions, and thus compressive stresses, into the glass surface. Like tempered glass, chemically strengthened glass is stronger in tension than annealed glass due to its residual surface stresses.

**Chapter 11, Problem 56**

What is an allotrope? Name as many carbon allotropes as you can.

**Chapter 11, Solution 56**

Allotrope is the structural form by which an element may exist. Some elements can exist in more than one structural form and thus have many allotropes. For carbon many solid allotropes exist including, graphite, diamond, bucky ball, bucky tube, and amorphous carbon.

**Chapter 11, Problem 57**

What is a Buckminster fullerene? What are some of its properties? Draw a schematic.

**Chapter 11, Solution 57**

Buckminster fullerene is the cage-like (soccer ball shape) cluster of carbon atoms forming a  $C_x$  molecule. It is named after Buckminster an architect who designed domes with similar structure to that of a fullerene. The fullerene molecule,  $C_{60}$ , has 60 carbon atoms attached to form pentagons and hexagons that form the cage-like structure (see Figure 11.14). The cluster has a diameter of 0.710 nm. The aggregate (the solid compact) has an FCC structure with clusters bonded together through van der Waals forces. The aggregate has similar lubricating characteristics as graphite.

**Chapter 11, Problem 58**

What is a carbon nanotube? What are some of its properties? Name some applications for nanotubes.

**Chapter 11, Solution 58**

It is tube like structure (cluster) of carbon atoms formed by hexagonal and pentagonal carbon sub-elements. The structure is similar to a graphite layer folded to form a tube with added end-caps. The diameter of the nano-tube is mostly 1.4 nm. Its length ranges from micrometer to millimeter. The nano-tube is believed to have strength 20 times higher than strongest steels ( $\sim 40$  GPa) with an incredibly high elastic modulus of 1.3 TPa. Applications include STM tips, field emitters, sensors, and fiber materials for fiber reinforced composites.

**Chapter 11, Problem 59**

Name five groups of ceramic coating materials.

**Chapter 11, Solution 59**

Glasses, oxides, carbides, silicides, borides and nitrides.

**Chapter 11, Problem 60**

Define the following terms: (a) glaze, (b) porcelain enamel, (c) glass enamel.

**Chapter 11, Solution 60**

- (a) Glaze – A glass coating applied to a ceramic substrate.
- (b) Porcelain enamel - A glass coating applied to a metal substrate.
- (c) Glass enamel - A glass coating applied to a glass substrate.

**Chapter 11, Problem 61**

How are glass coatings applied to various components?

**Chapter 11, Solution 61**

Glass coatings are applied through spraying or dipping techniques.

**Chapter 11, Problem 62**

Define agglomerates or aggregates in nanoceramic production.

**Chapter 11, Solution 62**

When the starting nanocrystalline powder (100 nm) is compacted, the powder has a tendency to bond and form bigger size particles. This is called agglomeration. Agglomerated powders do not pack as well and this is generally an undesirable effect.

**Chapter 11, Problem 63**

Using Pauling's equation (Eq. 2.10), compare the percent covalent character of the following compounds: hafnium carbide, titanium carbide, tantalum carbide, boron carbide, and silicon carbide.

**Chapter 11, Solution 63**

Recall that Pauling's equation gives the percent covalent character as:

$$\% \text{ covalent character} = e^{-0.25(X_A - X_B)^2} \times 100\%$$

Applying this equation, a table can be generated as follows.

Compound	Electronegativities		$(X_A - X_B)^2$	$-0.25(X_A - X_B)^2$	% Covalent Character
	$X_A$	$X_B$			
HfC	1.2	2.5	1.69	-0.4225	65.5
TiC	1.3	2.5	1.44	-0.360	69.8
TaC	1.4	2.5	1.21	-0.3025	73.9
BC	2.0	2.5	0.25	-0.0625	93.9
SiC	1.8	2.5	0.49	-0.1225	88.5

**Chapter 11, Problem 64**

Using Fig. 11.51, calculate the critical radius ratio for octahedral coordination.



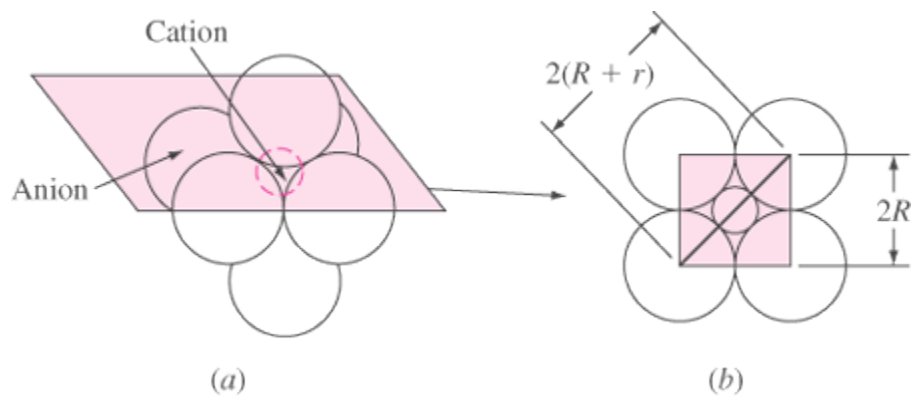


Figure 11.59

**Chapter 11, Solution 64**

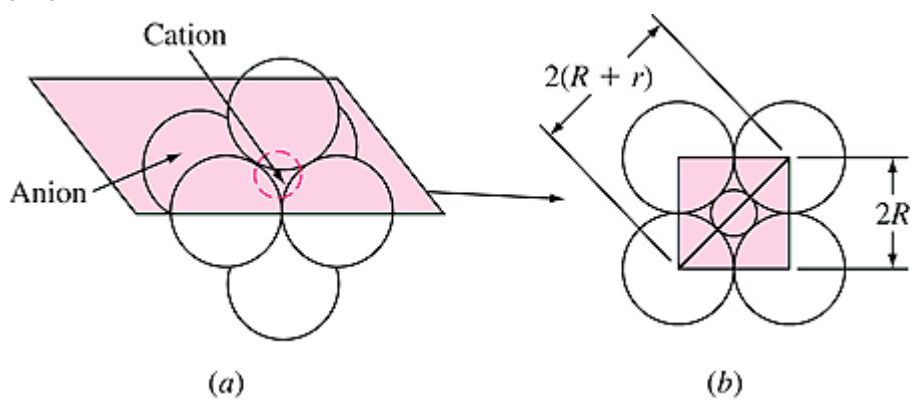


Figure 11.59 (a) Octahedral coordination of six anions (radii =  $R$ ) around a central cation of radius  $r$ . (b) Horizontal section through center of (a).

From the triangle shown above in Fig. 11.59 (b),

$$\begin{aligned}
[2(r + R)]^2 &= (2R)^2 + (2R)^2 \\
(r + R)^2 &= 2R^2 \\
r + R &= \sqrt{2}R \\
r &= \sqrt{2}R - R = 0.414R \\
\frac{r}{R} &= \mathbf{0.414}
\end{aligned}$$

### Chapter 11, Problem 65

Predict the coordination number for (a) BaO and (b) LiF. Ionic radii are  $\text{Ba}^{2+} = 0.143 \text{ nm}$ ,  $\text{O}^{2-} = 0.132 \text{ nm}$ ,  $\text{Li}^+ = 0.078 \text{ nm}$ ,  $\text{F}^- = 0.133 \text{ nm}$ .

### Chapter 11, Solution 65

(d) Using Appendix IV, the radius ratio for BaO is

$$\frac{r_{\text{cation}}}{r_{\text{anion}}} = \frac{r(\text{Ba}^{2+})}{R(\text{O}^{2-})} = \frac{0.143}{0.132} = 1.08$$

This ratio is greater than 0.732 and greater than 1.0. This is an unusual case in which the cation is larger than the anion because the elements respectively lie in Periods 6 and 2 of the periodic table. But if we invert this ratio to represent an anion surrounded by cations, we obtain 0.93. BaO should thus show cubic coordination (CN = 8). The solid is actually octahedral, CN = 6.

(e) Using Appendix IV, the radius ratio for LiF is

$$\frac{r_{\text{cation}}}{r_{\text{anion}}} = \frac{r(\text{Li}^+)}{R(\text{F}^-)} = \frac{0.078}{0.133} = 0.59$$

This ratio is greater than 0.414 and less than 0.732, thus LiF should have an octahedron coordination number, CN = 6, and it does.

### Chapter 11, Problem 66

Calculate the density in grams per cubic centimeter of CsI, which has the CsCl structure. Ionic radii are  $\text{Cs}^+ = 0.165 \text{ nm}$  and  $\text{I}^- = 0.220 \text{ nm}$ .

### Chapter 11, Solution 66

For the CsCl structure,  $\sqrt{3}a = 2(r + R)$ . Thus, the lattice constant measures,

$$a = \frac{2}{\sqrt{3}}(0.165 \text{ nm} + 0.220 \text{ nm}) = 0.445 \text{ nm} = 4.45 \times 10^{-8} \text{ cm}$$

Since the unit cell of CsI contains one  $\text{Cs}^+$  and one  $\text{I}^-$  ion, its mass is

$$m_{\text{unit cell}} = \frac{(1\text{Cs}^+ \times 132.9 \text{ g/mol}) + (1\text{I}^- \times 126.9 \text{ g/mol})}{6.02 \times 10^{23} \text{ ions/mol}} = 4.32 \times 10^{-22} \text{ g}$$

The density is thus calculated as,

$$\rho = \frac{m}{V} = \frac{m}{a^3} = \frac{4.32 \times 10^{-22} \text{ g}}{(4.45 \times 10^{-8} \text{ cm})^3} = 4.90 \text{ g/cm}^3$$

### Chapter 11, Problem 67

Calculate the density in grams per cubic centimeter of CsBr, which has the CsCl structure. Ionic radii are  $\text{Cs}^+ = 0.165 \text{ nm}$  and  $\text{Br}^- = 0.196 \text{ nm}$ .

**Chapter 11, Solution 67**

For the CsCl structure,  $\sqrt{3}a = 2(r + R)$ . Thus, the lattice constant is,

$$a = \frac{2}{\sqrt{3}}(0.165 \text{ nm} + 0.196 \text{ nm}) = 0.417 \text{ nm} = 4.17 \times 10^{-8} \text{ cm}$$

Since the unit cell of CsI contains one  $\text{Cs}^+$  and one  $\text{Br}^-$  ion, its mass is

$$m_{\text{unit cell}} = \frac{(1\text{Cs}^+ \times 132.9 \text{ g/mol}) + (1\text{Br}^- \times 79.90 \text{ g/mol})}{6.02 \times 10^{23} \text{ ions/mol}} = 3.53 \times 10^{-22} \text{ g}$$

The density is thus calculated as,

$$\rho = \frac{m}{V} = \frac{m}{a^3} = \frac{3.53 \times 10^{-22} \text{ g}}{(4.17 \times 10^{-8} \text{ cm})^3} = 4.87 \text{ g/cm}^3$$

**Chapter 11, Problem 68**

Calculate the linear densities in ions per nanometer in the [110] and [111] directions for (a) NiO and (b) CdO. Ionic radii are  $\text{Ni}^{2+} = 0.078 \text{ nm}$ ,  $\text{Cd}^{2+} = 0.103 \text{ nm}$ , and  $\text{O}^{2-} = 0.132 \text{ nm}$ .

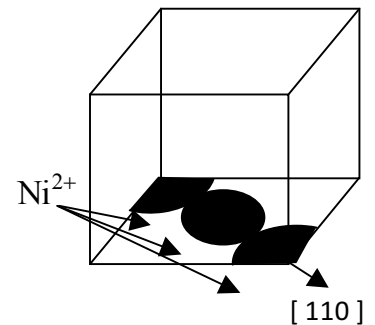
**Chapter 11, Solution 68**

Since NiO and CdO have the NaCl crystal structure,  $a = 2(r + R)$ .

(a) For NiO in the [110] direction,

$$a = 2(r_{\text{Ni}^{2+}} + R_{\text{O}^{2-}}) = 2(0.078 \text{ nm} + 0.132 \text{ nm}) = 0.420 \text{ nm}$$

$$\rho_L = \frac{2\text{Ni}^{2+}}{\sqrt{2}a} = \frac{2\text{Ni}^{2+}}{\sqrt{2}(0.420 \text{ nm})} = 3.37 \text{ Ni}^{2+}/\text{nm}$$

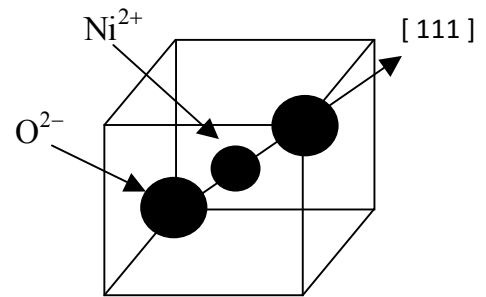


If we shift the origin from (0, 0, 0) to (0, ½, 0), we obtain

$$\rho_L = \frac{2\text{O}^{2-}}{\sqrt{2}a} = \frac{2\text{O}^{2-}}{\sqrt{2}(0.420 \text{ nm})} = \mathbf{3.37 \text{ O}^{2-}/\text{nm}}$$

For the [111] direction,

$$\rho_L = \frac{1\text{O}^{2-}}{\sqrt{3}a} = \frac{1\text{O}^{2-}}{\sqrt{3}(0.420 \text{ nm})} = \mathbf{1.37 \text{ O}^{2-}/\text{nm}}$$



$$\rho_L = \frac{1\text{Ni}^{2+}}{\sqrt{3}a} = \frac{1\text{Ni}^{2+}}{\sqrt{3}(0.420 \text{ nm})} = \mathbf{1.37 \text{ Ni}^{2+}/\text{nm}}$$

(b) For CdO in the [110] direction,

$$a = 2(r_{\text{Cd}^{2+}} + R_{\text{O}^{2-}}) = 2(0.103 \text{ nm} + 0.132 \text{ nm}) = 0.470 \text{ nm}$$

$$\rho_L = \frac{2\text{Cd}^{2+}}{\sqrt{2}a} = \frac{2\text{Cd}^{2+}}{\sqrt{2}(0.470 \text{ nm})} = \mathbf{3.01 \text{ Cd}^{2+}/\text{nm}}$$

Moving the origin from (0, 0, 0) to (0, ½, 0),

$$\rho_L = \frac{2\text{O}^{2-}}{\sqrt{2}a} = \frac{2\text{O}^{2-}}{\sqrt{2}(0.470 \text{ nm})} = \mathbf{3.01 \text{ O}^{2-}/\text{nm}}$$

For the [111] direction,

$$\rho_L = \frac{1\text{O}^{2-}}{\sqrt{3}a} = \frac{1\text{O}^{2-}}{\sqrt{3}(0.470 \text{ nm})} = \mathbf{1.23 \text{ O}^{2-}/\text{nm}}$$

$$\rho_L = \frac{1\text{Ni}^{2+}}{\sqrt{3}a} = \frac{1\text{Ni}^{2+}}{\sqrt{3}(0.470 \text{ nm})} = \mathbf{1.23 \text{ Ni}^{2+}/\text{nm}}$$

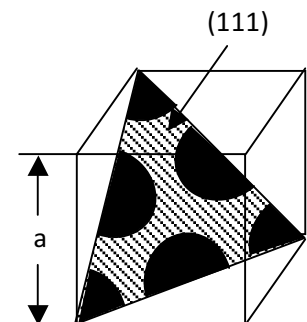
### Chapter 11, Problem 69

Calculate the planar densities in ions per square nanometer on the (111) and (110) planes for (a) CoO and (b) LiCl. Ionic radii are  $\text{Co}^{2+} = 0.082 \text{ nm}$ ,  $\text{O}^{2-} = 0.132 \text{ nm}$ ,  $\text{Li}^+ = 0.078 \text{ nm}$ , and  $\text{Cl}^- = 0.181 \text{ nm}$ .

### Chapter 11, Solution 69

First recognize that both CoO and LiCl have the NaCl structure.

- (a) For CoO, if we consider the  $\text{O}^{2-}$  anions to be located at the FCC positions of a cubic unit cell, then the (111) plane contains the equivalent of two anions.



$$3 \times \frac{1}{6} \text{ anion} + 3 \times \frac{1}{2} \text{ anion} = 2 \text{ anions}$$

The lattice constant is  $a = 2(r + R) = 2(0.082 \text{ nm} + 0.132 \text{ nm}) = 0.428 \text{ nm}$ . The area of the (111) plane is,

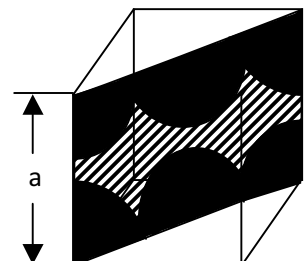
$$A_{(111)} = \frac{1}{2}bh = \frac{1}{2}(\sqrt{2}a)\left(\sqrt{\frac{3}{2}}a\right) = \frac{\sqrt{3}}{2}a^2 = \frac{\sqrt{3}}{2}(0.428 \text{ nm})^2 = 0.159 \text{ nm}^2$$

The planar density for the  $\text{O}^{2-}$  anions then becomes,

$$\rho_{\text{planar}} = \frac{2(\text{O}^{2-} \text{ ions})}{0.159 \text{ nm}^2} = \mathbf{12.6 \text{ O}^{2-} \text{ ions/nm}^2}$$

The planar density of the  $\text{Co}^{2+}$  cations is the same if we consider them to be located at the FCC lattice points of the unit cell. Consequently,

$$\rho_{\text{planar}}(\text{CoO}) = \mathbf{12.6 (\text{Co}^{2+} \text{ or } \text{O}^{2-}) \text{ ions/nm}^2}$$



For the (110) plane, we have two ions contained within the plane. The area of the plane is,

$$A_{(110)} = \frac{1}{2}bh = \frac{1}{2}(\sqrt{2}a)(a) = \frac{\sqrt{2}}{2}a^2 = \frac{\sqrt{2}}{2}(0.428 \text{ nm})^2 = 0.13 \text{ nm}^2$$

The (110) planar densities for CoO are,

$$\rho_{\text{planar}} = \frac{2(\text{O}^{2-} \text{ ions})}{0.13 \text{ nm}^2} = \mathbf{15.4 \text{ O}^{2-} \text{ ions/nm}^2}$$

$$\rho_{\text{planar}} = \frac{2(\text{Co}^{2+} \text{ ions})}{0.13 \text{ nm}^2} = \mathbf{15.4 \text{ Co}^{2+} \text{ ions/nm}^2}$$

(b) Similarly, for LiCl, the (111) planar densities are calculated as:

$$a = 2(r + R) = 2(0.078 \text{ nm} + 0.181 \text{ nm}) = 0.518 \text{ nm}$$

$$A_{(111)} = \frac{1}{2}bh = \frac{\sqrt{3}}{2}a^2 = \frac{\sqrt{3}}{2}(0.518 \text{ nm})^2 = 0.232 \text{ nm}^2$$

$$\rho_{\text{planar}} = \frac{2(\text{Cl}^- \text{ ions})}{0.232 \text{ nm}^2} = \mathbf{8.6 \text{ Cl}^- \text{ ions/nm}^2}$$

$$\rho_{\text{planar}} = \frac{2(\text{Li}^+ \text{ ions})}{0.232 \text{ nm}^2} = \mathbf{8.6 \text{ Li}^+ \text{ ions/nm}^2}$$



For the (110) plane,

$$A_{(110)} = \frac{1}{2}bh = \frac{\sqrt{2}}{2}a^2 = \frac{\sqrt{2}}{2}(0.518 \text{ nm})^2 = 0.19 \text{ nm}^2$$

$$\rho_{\text{planar}} = \frac{2(\text{Cl}^- \text{ ions})}{0.19 \text{ nm}^2} = \mathbf{10.5 \text{ Cl}^- \text{ ions/nm}^2}$$

$$\rho_{\text{planar}} = \frac{2(\text{Li}^+ \text{ ions})}{0.19 \text{ nm}^2} = \mathbf{10.5 \text{ Li}^+ \text{ ions/nm}^2}$$

**Chapter 11, Problem 70**

Calculate the density in grams per cubic centimeter of (a) SrO and (b) VO. Ionic radii are  $\text{V}^{2+} = 0.065 \text{ nm}$ ,  $\text{Co}^{2+} = 0.082 \text{ nm}$ , and  $\text{O}^{2-} = 0.132 \text{ nm}$ .

### Chapter 11, Solution 70

Both SrO and VO have the NaCl structure so  $a = 2(r + R)$  and there are four anions and four cations per unit cell.

(a) For SrO,

$$a = 2(r + R) = 2(0.127 \text{ nm} + 0.132 \text{ nm}) = 0.518 \text{ nm}$$

$$m_{\text{unit cell}} = \frac{(4\text{Sr}^{2+} \times 87.62 \text{ g/mol}) + (4\text{O}^{2-} \times 16.00 \text{ g/mol})}{6.02 \times 10^{23} \text{ ions/mol}} = 6.89 \times 10^{-22} \text{ g}$$

The density is thus calculated as,

$$\rho = \frac{m}{V} = \frac{m}{a^3} = \frac{6.89 \times 10^{-22} \text{ g}}{(5.18 \times 10^{-8} \text{ cm})^3} = \mathbf{4.96 \text{ g/cm}^3}$$

(b) For VO,

$$a = 2(r + R) = 2(0.065 \text{ nm} + 0.132 \text{ nm}) = 0.394 \text{ nm}$$

$$m_{\text{unit cell}} = \frac{(4\text{V}^{2+} \times 50.94 \text{ g/mol}) + (4\text{O}^{2-} \times 16.00 \text{ g/mol})}{6.02 \times 10^{23} \text{ ions/mol}} = 4.45 \times 10^{-22} \text{ g}$$

The density is thus,

$$\rho = \frac{m}{V} = \frac{m}{a^3} = \frac{4.45 \times 10^{-22} \text{ g}}{(3.94 \times 10^{-8} \text{ cm})^3} = \mathbf{7.27 \text{ g/cm}^3}$$

**Chapter 11, Problem 71**

Calculate the ionic packing factor for (a) MnO and (b) SrO. Ionic radii are  $\text{Mn}^{2+} = 0.091 \text{ nm}$ ,  $\text{Sr}^{2+} = 0.127 \text{ nm}$ , and  $\text{O}^{2-} = 0.132 \text{ nm}$ .

**Chapter 11, Solution 71**

Both MnO and SrO have the NaCl structure. Thus there are four anions and four cations per unit cell and the ionic packing factor is calculated using the equation:

$$\text{IPF} = \frac{\text{Vol. of ions per unit cell}}{\text{Vol. of unit cell}} = \frac{4\left(\frac{4}{3}\pi r^3\right) + 4\left(\frac{4}{3}\pi R^3\right)}{a^3} = \frac{16/3\pi(r^3 + R^3)}{a^3}$$

(a) For MnO,  $a = 2(0.091 \text{ nm} + 0.132 \text{ nm}) = 0.446 \text{ nm}$  and the IPF is

$$\text{IPF} = \frac{16/3\pi(r^3 + R^3)}{a^3} = \frac{16\pi[(0.091 \text{ nm})^3 + (0.132 \text{ nm})^3]}{3(0.446 \text{ nm})^3} = \mathbf{0.577}$$

(b) For SrO,  $a = 2(0.127 \text{ nm} + 0.132 \text{ nm}) = 0.518 \text{ nm}$  and the IPF is

$$\text{IPF} = \frac{16/3\pi(r^3 + R^3)}{a^3} = \frac{16\pi[(0.127 \text{ nm})^3 + (0.132 \text{ nm})^3]}{3(0.518 \text{ nm})^3} = \mathbf{0.524}$$

**Chapter 11, Problem 72**

ZnTe has the zinc blende crystal structure. Calculate the density of ZnTe. Ionic radii are  $\text{Zn}^{2+} = 0.083 \text{ nm}$  and  $\text{Te}^{2-} = 0.211 \text{ nm}$ .

**Chapter 11, Solution 72**

Since ZnTe has the zinc blende crystal structure (ZnS), there are four zinc ions and four tellurium ions per unit cell. Also, the lattice constant is calculated as  $a = \frac{4}{\sqrt{3}}(r + R)$ .

$$a = \frac{4}{\sqrt{3}}(r + R) = \frac{4}{\sqrt{3}}(0.083 \text{ nm} + 0.211 \text{ nm}) = 0.679 \text{ nm}$$

$$m_{\text{unit cell}} = \frac{(4\text{Zn}^{2+} \times 65.38 \text{ g/mol}) + (4\text{Te}^{2-} \times 127.6 \text{ g/mol})}{6.02 \times 10^{23} \text{ ions/mol}} = 1.28 \times 10^{-21} \text{ g}$$

The density is thus calculated as,

$$\rho = \frac{m}{V} = \frac{m}{a^3} = \frac{1.28 \times 10^{-21} \text{ g}}{(6.79 \times 10^{-8} \text{ cm})^3} = 4.09 \text{ g/cm}^3$$

### Chapter 11, Problem 73

BeO has the zinc blende crystal structure. Calculate the density of BeO. Ionic radii are  $\text{Be}^{2+} = 0.034 \text{ nm}$  and  $\text{O}^{2-} = 0.132 \text{ nm}$ .

### Chapter 11, Solution 73

Since BeO has the zinc blende crystal structure, there are four zinc ions and four oxygen ions per unit

cell. Also, the lattice constant is calculated as  $a = \frac{4}{\sqrt{3}}(r + R)$ .

$$a = \frac{4}{\sqrt{3}}(r + R) = \frac{4}{\sqrt{3}}(0.034 \text{ nm} + 0.132 \text{ nm}) = 0.383 \text{ nm}$$

$$m_{\text{unit cell}} = \frac{(4\text{Be}^{2+} \times 9.012 \text{ g/mol}) + (4\text{O}^{2-} \times 16.00 \text{ g/mol})}{6.02 \times 10^{23} \text{ ions/mol}} = 1.66 \times 10^{-22} \text{ g}$$

The density is thus calculated as,

$$\rho = \frac{m}{V} = \frac{m}{a^3} = \frac{1.66 \times 10^{-22} \text{ g}}{(3.83 \times 10^{-8} \text{ cm})^3} = 2.95 \text{ g/cm}^3$$

**Chapter 11, Problem 74**

Calculate the density in grams per cubic centimeter of  $\text{ZrO}_2$ , which has the  $\text{CaF}_2$  crystal structure. Ionic radii are  $\text{Zr}^{4+} = 0.087 \text{ nm}$  and  $\text{O}^{2-} = 0.132 \text{ nm}$ .

**Chapter 11, Solution 74**

Since  $\text{ZrO}_2$  has the  $\text{CaF}_2$  crystal structure, there are four  $\text{Zr}^{4+}$  ions and eight  $\text{O}^{2-}$  ions per unit cell. Also, the lattice constant is calculated as  $a = \frac{4}{\sqrt{3}}(r + R)$ .

$$a = \frac{4}{\sqrt{3}}(r + R) = \frac{4}{\sqrt{3}}(0.087 \text{ nm} + 0.132 \text{ nm}) = 0.506 \text{ nm}$$

$$m_{\text{unit cell}} = \frac{(4\text{Zr}^{2+} \times 91.22 \text{ g/mol}) + (8\text{O}^{2-} \times 16.00 \text{ g/mol})}{6.02 \times 10^{23} \text{ ions/mol}} = 8.19 \times 10^{-22} \text{ g}$$

The density is thus calculated as,

$$\rho = \frac{m}{V} = \frac{m}{a^3} = \frac{8.19 \times 10^{-22} \text{ g}}{(5.06 \times 10^{-8} \text{ cm})^3} = 6.32 \text{ g/cm}^3$$

**Chapter 11, Problem 75**

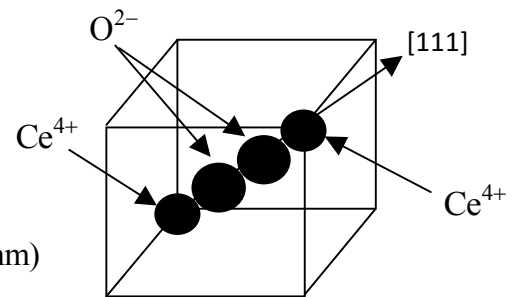
Calculate the linear density in ions per nanometer in the [111] and [110] directions for  $\text{CeO}_2$ , which has the fluorite structure. Ionic radii are  $\text{Ce}^{4+} = 0.102 \text{ nm}$  and  $\text{O}^{2-} = 0.132 \text{ nm}$ .

**Chapter 11, Solution 75**

For  $\text{CeO}_2$  in the [111] direction, there are two  $\text{O}^{2-}$  and one

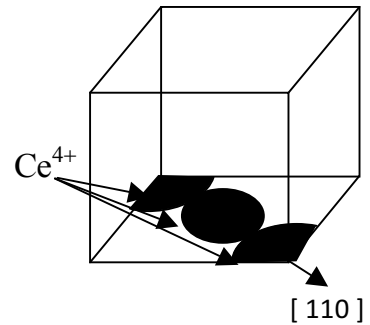
$\text{Ce}^{4+}$  along the cube diagonal, which is  $\sqrt{3}a$  in length

$$\begin{aligned} a &= \frac{4}{\sqrt{3}}(r_{\text{Ce}^{4+}} + R_{\text{O}^{2-}}) = \frac{4}{\sqrt{3}}(0.102 \text{ nm} + 0.132 \text{ nm}) \\ &= 0.540 \text{ nm} \end{aligned}$$



$$\rho_L = \frac{1\text{Ce}^{4+} + 2\text{O}^{2-}}{\sqrt{3}a} = \frac{1\text{Ce}^{4+} + 2\text{O}^{2-}}{\sqrt{3}(0.540 \text{ nm})}$$

$$= (1.07\text{Ce}^{4+} + 2.14 \text{O}^{2-})/\text{nm}$$



For the [110] direction,

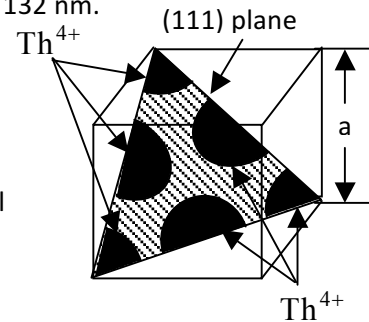
$$\rho_L = \frac{2\text{Ce}^{4+}}{\sqrt{2}a} = \frac{2\text{Ce}^{4+}}{\sqrt{2}(0.540 \text{ nm})} = 2.62 \text{ Ce}^{4+}/\text{nm}$$

### Chapter 11, Problem 76

Calculate the planar density in ions per square nanometer in the (111) and (110) planes of  $\text{ThO}_2$ , which has the fluorite structure. Ionic radii are  $\text{Th}^{4+} = 0.110 \text{ nm}$  and  $\text{O}^{2-} = 0.132 \text{ nm}$ .

### Chapter 11, Solution 76

If we consider the  $\text{Th}^{4+}$  cations to be located at the FCC positions of a cubic unit cell, and the  $\text{O}^{2-}$  anions in the tetrahedral interstitial sites, then the (111) plane contains the equivalent of two cations.



$$3 \times \frac{1}{6} \text{ cation} + 3 \times \frac{1}{2} \text{ cation} = 2 \text{ cations}$$

The lattice constant is  $a = \frac{4}{\sqrt{3}}(r_{\text{Th}^{4+}} + R_{\text{O}^{2-}}) = \frac{4}{\sqrt{3}}(0.110 \text{ nm} + 0.132 \text{ nm}) = 0.559 \text{ nm}$ .

The area of the (111) plane is,

$$A_{(111)} = \frac{1}{2}bh = \frac{1}{2}(\sqrt{2}a)\left(\sqrt{\frac{3}{2}}a\right) = \frac{\sqrt{3}}{2}a^2 = \frac{\sqrt{3}}{2}(0.559 \text{ nm})^2 = 0.270 \text{ nm}^2$$

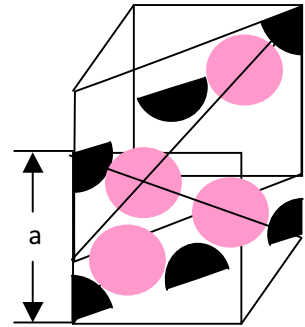
The planar density for the  $\text{Th}^{4+}$  cations on the (111) plane is thus,

$$\rho_{\text{planar}} = \frac{2(\text{Th}^{4+} \text{ ions})}{0.270 \text{ nm}^2} = \mathbf{7.4 \text{ Th}^{4+} \text{ ions/nm}^2}$$

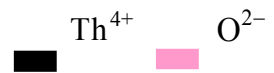
For the (110) plane, we have two ions contained within the plane.

The area of the plane is,

$$\begin{aligned} A_{(110)} &= \frac{1}{2}bh = \frac{1}{2}(\sqrt{2}a)(a) = \frac{\sqrt{2}}{2}a^2 = \frac{\sqrt{2}}{2}(0.559 \text{ nm})^2 \\ &= 0.221 \text{ nm}^2 \end{aligned}$$



The (110) planar densities for  $\text{ThO}_2$  are,



$$\rho_{\text{planar}} = \frac{4(\text{O}^{2-} \text{ ions})}{0.221 \text{ nm}^2} = 18.1 \text{ O}^{2-} \text{ ions/nm}^2$$

$$\rho_{\text{planar}} = \frac{2(\text{Th}^{4+} \text{ ions})}{0.221 \text{ nm}^2} = 9.1 \text{ Th}^{4+} \text{ ions/nm}^2$$

$$\rho_{\text{planar}}(\text{ThO}_2) = \mathbf{18.1 \text{ O}^{2-} \text{ or } 9.1 \text{ Th}^{4+} \text{ ions/nm}^2}$$

### Chapter 11, Problem 77

Calculate the ionic packing factor for  $\text{SrF}_2$ , which has the fluorite structure. Ionic radii are  $\text{Sr}^{2+} = 0.127 \text{ nm}$  and  $\text{F}^- = 0.133 \text{ nm}$ .

**Chapter 11, Solution 77**

$$\text{IPF} = \frac{\text{Vol. of ions per unit cell}}{\text{Vol. of unit cell}} = \frac{(\frac{4}{3}\pi) \left[ (4r_{\text{Sr}^{2+}}^3) + (8R_{\text{F}^-}^3) \right]}{a^3}$$

where  $a = \frac{4}{\sqrt{3}}(0.127 \text{ nm} + 0.133 \text{ nm}) = 0.600 \text{ nm}$ . Substituting,

$$\text{IPF} = \frac{4\pi \left[ 4(0.127 \text{ nm})^3 + 8(0.133 \text{ nm})^3 \right]}{3(0.600 \text{ nm})^3} = \mathbf{0.524}$$

$$\rho_{\text{planar}} = \frac{4(\text{O}^{2-} \text{ ions})}{0.221 \text{ nm}^2} = 18.1 \text{ O}^{2-} \text{ ions/nm}^2$$

$$\rho_{\text{planar}} = \frac{2(\text{Th}^{4+} \text{ ions})}{0.221 \text{ nm}^2} = 9.1 \text{ Th}^{4+} \text{ ions/nm}^2$$

$$\rho_{\text{planar}}(\text{ThO}_2) = \mathbf{18.1 \text{ O}^{2-} \text{ or } 9.1 \text{ Th}^{4+} \text{ ions/nm}^2}$$

**Chapter 11, Problem 78**

Why are only two-thirds of the octahedral interstitial sites filled by  $\text{Al}^{3+}$  ions when the oxygen ions occupy the HCP lattice sites in  $\text{Al}_2\text{O}_3$ ?

**Chapter 11, Solution 78**

When the oxygen ions occupy the HCP lattice sites in  $\text{Al}_2\text{O}_3$ , only two-thirds of the octahedral interstitial sites are filled by  $\text{Al}^{3+}$  ions in order to maintain electrical neutrality. There can only be two  $\text{Al}^{3+}$  ions for every three  $\text{O}^{2-}$  ions.



**Chapter 11, Problem 79**

Calculate the ionic packing factor for  $\text{CaTiO}_3$ , which has the perovskite structure. Ionic radii are  $\text{Ca}^{2+} = 0.106 \text{ nm}$ ,  $\text{Ti}^{4+} = 0.064 \text{ nm}$ , and  $\text{O}^{2-} = 0.132 \text{ nm}$ . Assume the lattice constant  $a = 2(r_{\text{Ti}^{4+}} + r_{\text{O}^{2-}})$ .

**Chapter 11, Solution 79**

In the perovskite structure, there are a total of one calcium ion, one titanium ion, and three oxygen atoms. The ionic packing factor is therefore calculated as,

$$\text{IPF} = \frac{\text{Vol. of ions per unit cell}}{\text{Vol. of unit cell}} = \frac{\left(\frac{4}{3}\pi\right)\left[\left(r_{\text{Ca}^{2+}}^3\right) + \left(r_{\text{Ti}^{4+}}^3\right) + \left(3r_{\text{O}^{2-}}^3\right)\right]}{a^3}$$

where  $a = 2(r_{\text{Ti}^{4+}} + r_{\text{O}^{2-}}) = 2(0.064 \text{ nm} + 0.132 \text{ nm}) = 0.392 \text{ nm}$ . Substituting,

$$\text{IPF} = \frac{4\pi\left[(0.106 \text{ nm})^3 + (0.064 \text{ nm})^3 + 3(0.132 \text{ nm})^3\right]}{3(0.392 \text{ nm})^3} = \mathbf{0.581}$$

**Chapter 11, Problem 80**

Calculate the density in grams per cubic centimeter of  $\text{SrSnO}_3$ , which has the perovskite structure. Ionic radii are  $\text{Sr}^{2+} = 0.127 \text{ nm}$ ,  $\text{Sn}^{4+} = 0.074 \text{ nm}$ , and  $\text{O}^{2-} = 0.132 \text{ nm}$ . Assume  $a = 2(r_{\text{Sn}^{4+}} + r_{\text{O}^{2-}})$ .

**Chapter 11, Solution 80**

For  $a = 2(r_{\text{Sn}^{4+}} + r_{\text{O}^{2-}}) = 2(0.074 \text{ nm} + 0.132 \text{ nm}) = 0.412 \text{ nm}$ , and a unit cell mass of

$$\begin{aligned} m_{\text{unit cell}} &= \frac{(1\text{Sr}^{2+} \times 87.62 \text{ g/mol}) + (1\text{Sn}^{4+} \times 118.7 \text{ g/mol}) + (3\text{O}^{2-} \times 16.00 \text{ g/mol})}{6.02 \times 10^{23} \text{ ions/mol}} \\ &= 4.22 \times 10^{-22} \text{ g} \end{aligned}$$

The density is thus calculated as,

$$\rho = \frac{m}{V} = \frac{m}{a^3} = \frac{4.22 \times 10^{-22} \text{ g}}{(4.12 \times 10^{-8} \text{ cm})^3} = 6.03 \text{ g/cm}^3$$

**Chapter 11, Problem 81**

Determine the composition of the ternary compound at point y in Fig. 11.30.

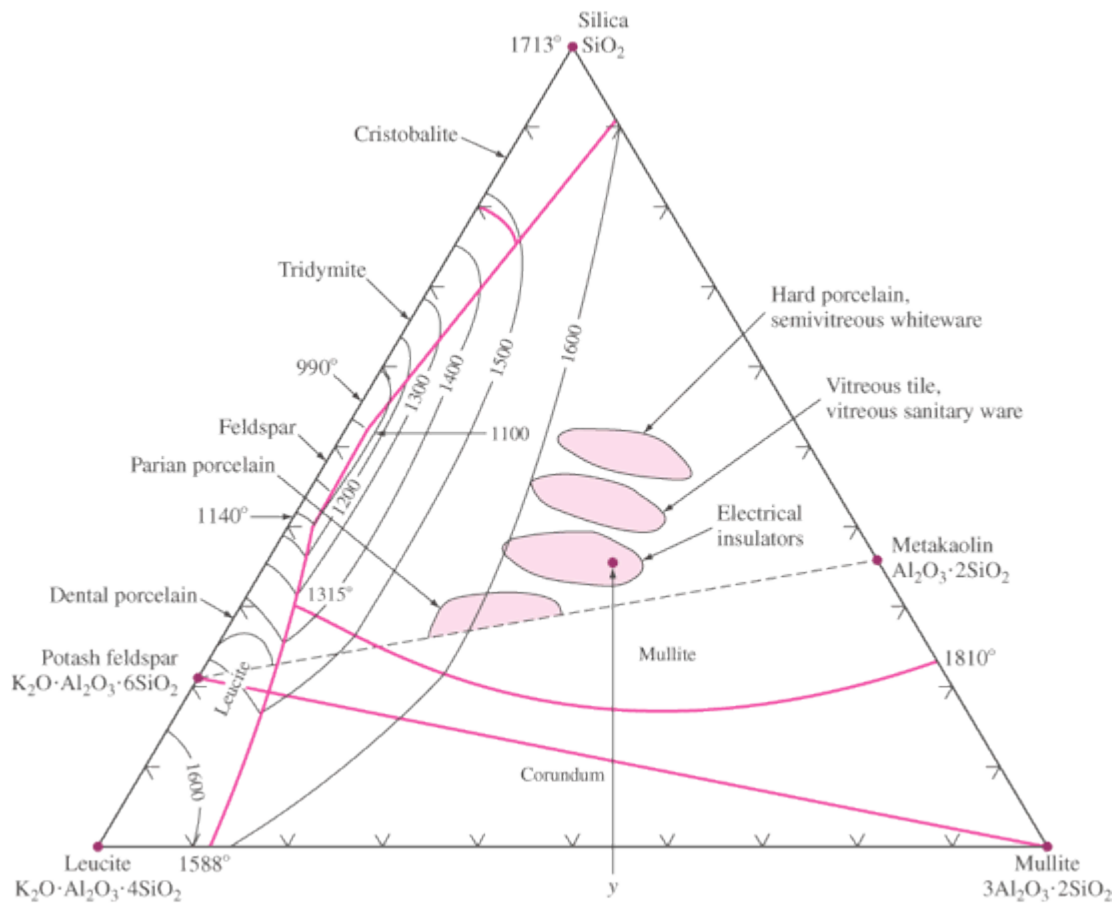


Figure 11.30

**Chapter 11, Solution 81**

At point y, the ternary compound has the composition 27 percent leucite, 36 percent silica, and 37 percent mullite.

**Chapter 11, Problem 82**

Why are triaxial porcelains not satisfactory for use at high frequencies?

**Chapter 11, Solution 82**

Triaxial porcelains are not satisfactory insulators for high frequency applications because dielectric losses become too large.

**Chapter 11, Problem 83**

What kinds of ions cause an increase in the conductivity of electrical porcelain?

**Chapter 11, Solution 83**

Alkali ions cause an increase in the conductivity of electrical porcelain.

**Chapter 11, Problem 84**

What is the composition of most technical ceramics?

**Chapter 11, Solution 84**

Most technical ceramics are composed of pure compounds or nearly pure compounds of chiefly oxides, carbides and nitrides.

**Chapter 11, Problem 85**

How are pure single-compound technical ceramic particles processed to produce a solid product? Give an example.

**Chapter 11, Solution 85**

Technical ceramics are typically cold or hot-pressed and then subjected to a process, such as sintering or reaction bonding, so that bonding can occur. Examples of technical ceramic are silicon nitride, alumina, silicon carbide and zirconia.

**Chapter 11, Problem 86**

What causes the lack of plasticity in crystalline ceramics?

**Chapter 11, Solution 86**

The lack of plasticity in crystalline ceramics is attributed to their ionic and covalent chemical bonds. In covalent crystals and covalently bonded ceramics, atoms bond through the exchange of electron charge between pairs of electrons, in a specific and directional manner. Consequently, if the ceramic is sufficiently stressed, electron-pair bonds undergo irreparable separation, causing the material to experience brittle fracture.

**Chapter 11, Problem 87**

Explain the plastic deformation mechanism for some single-crystal ionic solids such as NaCl and MgO. What is the preferred slip system?

**Chapter 11, Solution 87**

For some single-crystal ionic solids, such as NaCl and MgO, compressive stresses at room temperature cause considerable plastic deformation prior to fracture because planes of oppositely charged ions can slip relative to each other. These slip planes, which maintain their attraction through coulombic forces, typically prefer the  $\{110\}\langle 110\rangle$  slip system for NaCl-type structures.

**Chapter 11, Problem 88**

What structural defects are the main cause of failure of polycrystalline ceramic materials?

**Chapter 11, Solution 88**

Brittle fracture of polycrystalline ceramics is principally caused by one of four structural defects: cracks produced during surface finishing; voids; inclusions; and large grains produced during processing.

**Chapter 11, Problem 89**

How do (a) porosity and (b) grain size affect the tensile strength of ceramic materials?

**Chapter 11, Solution 89**

- (f) Pores serve as a source for stress induced crack initiation/propagation and reduce the cross-sectional area available for load application. Consequently, as the porosity of a ceramic material increases, the material tensile strength decreases.
  
- (g) For a porosity-free ceramic, the flaw size, and thus the strength, is solely a function of grain size; the finer the grain size, the smaller the flaws at grain boundaries and the greater the ceramic tensile strength.

**Chapter 11, Problem 90**

A reaction-bonded silicon nitride ceramic has a strength of 250 MPa and a fracture toughness of 3.4

$\rho = \frac{m}{V} = \frac{128 \times 10^{-21} \text{ g}}{(6.79 \times 10^{-8} \text{ cm})^3} = 4.09 \text{ g/cm}^3$ . What is the largest-sized internal flaw that this material can support without fracturing? (Use  $Y = 1$  in the fracture-toughness equation.)

**Chapter 11, Solution 90**

$$\rho = \frac{m}{V} = \frac{m}{a^3} = \frac{4.45 \times 10^{-22} \text{ g}}{(3.94 \times 10^{-8} \text{ cm})^3} = 7.27 \text{ g/cm}^3$$

Thus the largest internal flaw is  $2a = 2(58.9 \text{ } \mu\text{m}) = 117.8 \text{ } \mu\text{m}$ .

**Chapter 11, Problem 91**

The maximum-sized internal flaw in a hot-pressed silicon carbide ceramic is  $25 \text{ } \mu\text{m}$ . If this material has a fracture toughness of  $3.7 \text{ MPa}\sqrt{\text{m}}$ , what is the maximum stress that this material can support? (Use  $Y = \sqrt{\pi}$ .)

**Chapter 11, Solution 91**

$$\sigma_f = \frac{1}{\sqrt{\pi a}} \left( \frac{K_{IC}}{Y} \right) = \frac{1}{\sqrt{\pi(2.5 \times 10^{-5} \text{ m})}} \left( \frac{3.7 \text{ MPa}\sqrt{\text{m}}}{\sqrt{\pi}} \right) = 236 \text{ MPa}$$

**Chapter 11, Problem 92**

A partially stabilized zirconia advanced ceramic has a strength of  $352 \text{ MPa}$  and a fracture toughness of  $7.5 \text{ MPa}\sqrt{\text{m}}$ . What is the largest-sized internal flaw (expressed in micrometers) that this material can support? (Use  $Y = \sqrt{\pi}$ .)

**Chapter 11, Solution 92**

$$a = \frac{1}{\pi} \left( \frac{K_{IC}}{Y\sigma_f} \right)^2 = \frac{1}{\pi} \left[ \frac{7.5 \text{ MPa}\sqrt{\text{m}}}{\sqrt{\pi}(352 \text{ MPa})} \right]^2 = \left[ \frac{7.5 \text{ MPa}\sqrt{\text{m}}}{\pi(352 \text{ MPa})} \right]^2 = 4.60 \times 10^{-5} \text{ m} = 46.0 \text{ } \mu\text{m}$$

Thus the largest internal flaw is  $2a = 2(46.0 \text{ } \mu\text{m}) = 92.0 \text{ } \mu\text{m}$ .

### Chapter 11, Problem 93

A fully stabilized, cubic polycrystalline  $ZrO_2$  sample has a fracture toughness of  $K_{IC} = 3.8 \text{ MPa}\sqrt{\text{m}}$  when tested on a four-point bend test.

(a) If the sample fails at a stress of 450 MPa, what is the size of the largest surface flaw? Assume  $Y = \sqrt{\pi}$ .

(b) The same test is performed with a partially stabilized  $ZrO_2$  specimen. This material is transformation-toughened and has a  $K_{IC} = 12.5 \text{ MPa}\sqrt{\text{m}}$ . If this material has the same flaw distribution as the fully stabilized sample, what stress must be applied to cause failure?

### Chapter 11, Solution 93

(a) The largest edge or surface crack is equal to  $a$  :

$$a = \frac{1}{\pi} \left( \frac{K_{IC}}{Y\sigma_f} \right)^2 = \left[ \frac{3.8 \text{ MPa}\sqrt{\text{m}}}{\pi(450 \text{ MPa})} \right]^2 = 7.23 \times 10^{-6} \text{ m} = 7.23 \mu\text{m}$$

(b) The stress which will cause failure is:

$$\sigma_f = \frac{1}{\sqrt{\pi a}} \left( \frac{K_{IC}}{\sqrt{\pi}} \right) = \frac{1}{\pi} \left( \frac{12.5 \text{ MPa}\sqrt{\text{m}}}{\sqrt{7.23 \times 10^{-6} \text{ m}}} \right) = 1480 \text{ MPa}$$

### Chapter 11, Problem 94

How does the specific volume versus temperature plot for a glass differ from that for a crystalline material when these materials are cooled from the liquid state?

### Chapter 11, Solution 94

The plot of specific volume versus temperature for a glass differs from that of a crystalline material in two ways. First, the glass does not experience a rapid decrease in specific volume at a temperature associated with a melting point; the glass cooling curve conveys a gradual decrease in specific volume throughout the cooling range. Second, the glass curve contains a marked decrease in slope at a glass transition temperature which other ceramics do not possess.

**Chapter 11, Problem 95**

How does the silica network of a simple silica glass differ from crystalline (cristobalite) silica?

**Chapter 11, Solution 95**

In a simple glass, the tetrahedra are joined corner to corner, forming a loose network. In contrast, a crystalline material, such as cristobalite, has Si-O tetrahedra joined corner to corner in a regular arrangement, producing a network having a long-range order.

**Chapter 11, Problem 96**

How is it possible for  $\text{BO}_3^{3-}$  triangles to be converted to  $\text{BO}_4^{4-}$  tetrahedral and still maintain neutrality in some borosilicate glasses?

**Chapter 11, Solution 96**

$\text{BO}_3^{3-}$  triangles can be converted to  $\text{BO}_4^{4-}$  tetrahedra by adding alkali and alkaline earth oxides whose cations provide the necessary electroneutrality.

**Chapter 11, Problem 97**

What are glass network modifiers? How do they affect the silica-glass network? Why are they added to silica glass?

**Chapter 11, Solution 97**

Glass network modifiers are oxides that break up the glass network. Examples include  $\text{Na}_2\text{O}$ ,  $\text{K}_2\text{O}$ ,  $\text{CaO}$ , and  $\text{MgO}$ . These oxides affect the silica glass network by breaking the network at the tetrahedra points. As a result, the tetrahedra have oxygen atoms with an unshared electron while the oxide's metal cations remain as ions ionically bonded in the network interstices. Glass modifiers are added to silica glass to facilitate forming and working the glass by lowering its viscosity.

**Chapter 11, Problem 98**

What are glass intermediate oxides? How do they affect the silica-glass network? Why are they added to silica glass?

**Chapter 11, Solution 98**

Glass intermediate oxides are oxides that cannot form a glass network by themselves but can join an existing one. These oxides may act as modifiers of the structure as well as become a part of the network chain. In the latter case, they sometimes leave the network deficient in electrons and alkali cations must be added for electrical neutrality. The intermediate oxides are added to glass to obtain special

properties. For example, large amounts (60 percent) of lead oxide can be added to produce an ornamental glass of great brilliance.

**Chapter 11, Problem 99**

What is the purpose of (a) MgO and (b) Al<sub>2</sub>O<sub>3</sub> additions to soda-lime glass?

**Chapter 11, Solution 99**

- (h) MgO is added to soda-lime glass in small quantities of 1 to 4 percent to prevent devitrification.
- (i) Al<sub>2</sub>O<sub>3</sub> is added in quantities of 0.5 to 1.5 percent to increase durability.

**Chapter 11, Problem 100**

Distinguish between hard and soft glasses and long and short glasses.

**Chapter 11, Solution 100**

A hard glass has a high softening point as compared to a soft glass. Long glasses have large temperature differences between their softening and strain points; they solidify more slowly than a short glass as the temperature decreases.

**Chapter 11, Problem 101**

A soda-lime plate glass between 500°C (strain point) and 700°C (softening point) has viscosities between  $10^{14.2}$  and  $10^{7.5}$  P, respectively. Calculate a value for the activation energy in this temperature region.

**Chapter 11, Solution 101**

First, convert the temperatures to absolute values:

$$\text{Strain point} = T_{stp} = 500^\circ\text{C} + 273 = 773 \text{ K}$$

$$\text{Softening point} = T_{sp} = 700^\circ\text{C} + 273 = 973 \text{ K}$$

Using Eq. 10.5,  $\eta_{stp} = \eta_0 e^{Q/RT_{stp}}$  and  $\eta_{sp} = \eta_0 e^{Q/RT_{sp}}$ . Dividing these equations and substituting the temperature and viscosity data,



$$\frac{\eta_{stp}}{\eta_{sp}} = \exp\left[\frac{Q}{R}\left(\frac{1}{T_{stp}} - \frac{1}{T_{sp}}\right)\right]$$

$$\frac{10^{14.2} \text{ P}}{10^{7.5} \text{ P}} = \exp\left[\frac{Q}{8.314 \text{ J/mol}\cdot\text{K}}\left(\frac{1}{723 \text{ K}} - \frac{1}{923 \text{ K}}\right)\right]$$

$$10^{6.7} = \exp\left[(3.605 \times 10^{-5})Q\right]$$

$$\ln 10^{6.7} = (3.605 \times 10^{-5})Q$$

$$Q = 4.28 \times 10^5 \text{ J/mol} = \mathbf{428 \text{ kJ/mol}}$$

### Chapter 11, Problem 102

A soda-lime glass has a viscosity of  $10^{14.6}$  P at  $560^\circ\text{C}$ . What will be its viscosity at  $675^\circ\text{C}$  if the activation energy for viscous flow is  $430 \text{ kJ/mol}$ ?

### Chapter 11, Solution 102

Let  $\eta_1 = \eta_0 e^{Q/RT_1}$  and  $\eta_2 = \eta_0 e^{Q/RT_2}$  where  $T_1 = 833 \text{ K}$  and  $T_2 = 948 \text{ K}$ . Then,

$$\frac{\eta_1}{\eta_2} = \exp\left[\frac{Q}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)\right]$$

$$\frac{10^{14.6} \text{ P}}{\eta_2} = \exp\left[\frac{430 \times 10^3 \text{ J/mol}}{8.314 \text{ J/mol}\cdot\text{K}}\left(\frac{1}{833 \text{ K}} - \frac{1}{948 \text{ K}}\right)\right]$$

$$\frac{10^{14.6} \text{ P}}{\eta_2} = \exp(7.532) = 1866.6$$

$$\eta_2 = 2.133 \times 10^{11} \text{ P} = \mathbf{10^{11.329} \text{ P} \approx 10^{11.33} \text{ P}}$$

### Chapter 11, Problem 103

A soda-lime glass has a viscosity of  $10^{14.3}$  P at  $570^\circ\text{C}$ . At what temperature will its viscosity be  $10^{9.9}$  P if the activation energy for the process is  $430 \text{ kJ/mol}$ ?

### Chapter 11, Solution 103

Let  $\eta_1 = \eta_0 e^{Q/RT_1}$  and  $\eta_2 = \eta_0 e^{Q/RT_2}$  where  $T_1 = 843 \text{ K}$ . Then,

$$\frac{\eta_1}{\eta_2} = \exp\left[\frac{Q}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)\right]$$

$$\frac{10^{14.3} \text{ P}}{10^{9.9} \text{ P}} = \exp\left[\frac{430 \times 10^3 \text{ J/mol}}{8.314 \text{ J/mol} \cdot \text{K}}\left(\frac{1}{843 \text{ K}} - \frac{1}{T_2}\right)\right]$$

$$\ln 10^{4.4} = \left[51,720\left(\frac{1}{843 \text{ K}} - \frac{1}{T_2}\right)\right]$$

$$T_2 = (0.0011862 - 0.0001959)^{-1} = \mathbf{1009.7 \text{ K} = 736.7^\circ\text{C}}$$

### Chapter 11, Problem 104

A borosilicate glass between 600°C (annealing point) and 800°C (softening point) has viscosities of  $10^{12.5}$  P and  $10^{7.4}$  P, respectively. Calculate a value for the activation energy for viscous flow in this region, assuming the equation  $\eta = \eta_0 e^{Q/RT}$  is valid.

### Chapter 11, Solution 104

$$\frac{\eta_{ap}}{\eta_{sp}} = \exp\left[\frac{Q}{R}\left(\frac{1}{T_{ap}} - \frac{1}{T_{sp}}\right)\right]$$

$$\frac{10^{12.5} \text{ P}}{10^{7.4} \text{ P}} = \exp\left[\frac{Q}{8.314 \text{ J/mol} \cdot \text{K}}\left(\frac{1}{873 \text{ K}} - \frac{1}{1073 \text{ K}}\right)\right]$$

$$10^{5.1} = \exp\left[(2.568 \times 10^{-5})Q\right]$$

$$\ln 10^{5.1} = (2.568 \times 10^{-5})Q$$

$$Q = 4.573 \times 10^5 \text{ J/mol} = \mathbf{457.3 \text{ kJ/mol}}$$

### Chapter 11, Problem 105

Discuss mechanical, electrical, and thermal properties of diamond. In each case, explain the behavior in terms of its atomic structure.

### Chapter 11, Solution 105

Diamond is the hardest nature-made material. The hardness of all other materials is referenced to diamond. This is the case because of its network-covalent atomic structure.

Diamond is an excellent electrical insulator because all valence electrons are tightly held in place by covalent bonds. These electrons cannot become active in the conduction process under normal conditions.

Diamond is an excellent conductor of heat. This is the case because of tight packing and the network covalent structure. Thermal vibrations of atoms travel easily across the lattice due to tight packing.

#### **Chapter 11, Problem 106**

Discuss the challenges in producing bulk nanocrystalline ceramics?

#### **Chapter 11, Solution 106**

The main challenges are to start with non-agglomerated powder and to optimize the sintering temperature and sintering time to avoid formation of large agglomerates.

#### **Chapter 11, Problem 107**

Why is the HIP process suitable for synthesizing nanocrystalline ceramics?

#### **Chapter 11, Solution 107**

The HIP process will shrink the available pores through compaction pressure. The pore shrinkage in HIP is non-diffusional and is due to plastic deformation of the nano-crystals. This is the case because nano-ceramics are ductile at elevated temperatures (due to superplasticity effect).

#### **Chapter 11, Problem 108**

Tensile property data of ceramic materials show more scatter than metals. Can you explain why?

#### **Chapter 11, Solution 108**

The reason for more scatter in the tensile property data of ceramics (compared to metals) is that ceramics are significantly more sensitive to minor surface flaws and voids. Ceramics are more brittle and more notch sensitive.

Pores, defects and voids are sources (regions) of stress concentration which could initiate crack growth at stress levels lower than normal.

### Chapter 11, Problem 109

(a) Discuss the advantages and disadvantages of using advanced ceramics in the structure of internal combustion engines. (b) Propose some methods of overcoming the shortcomings of ceramics for this application.

### Chapter 11, Solution 109

a). Advantages: high temperature strength, lighter weight (lower density than metals), wear resistant, chemically stable (even at high temperatures), low contact friction (less need for lubrication).

Disadvantages: brittle, low toughness, more expensive, hard to manufacture complex shapes. If ceramics were not brittle or had higher toughness, they would be the perfect material for use in engines.

b). It is possible to create metal-ceramic composites. The ductility of the metals will increase the toughness of the ceramic. For instance, tungsten-silicon carbide composite.

Place metal on the ceramic compact and apply heat to melt the metal. Metal (molten) will diffuse through the pores and solidify when cooled.

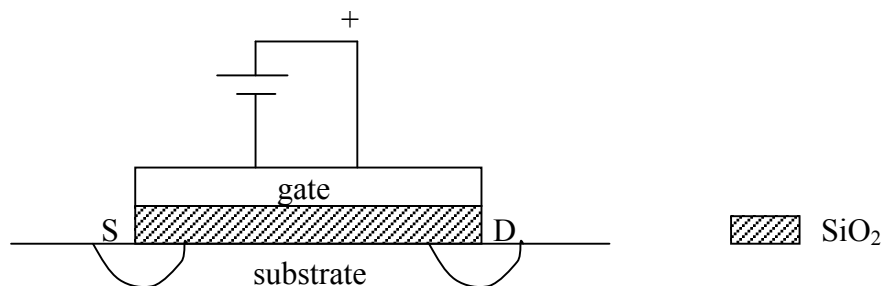
### Chapter 11, Problem 110

Investigate the application of ceramics in the electronic industry. (a) What are these applications? (b) Why are ceramics selected?

### Chapter 11, Solution 110

a) Ceramics such as  $\text{SiO}_2$  are routinely used in computer chips and ICs.

b) Ceramics serve mostly as insulators to assure that there is no contact between the gate (usually a metal) and the substrate (semiconductor).



Ceramics are selected because of their outstanding insulative properties due to their ionic/covalent bonds.

### Chapter 11, Problem 111

For insulation purposes, you would like to cover the surface of a substrate with an extremely thin layer of  $\text{Si}_3\text{N}_4$ . (a) Propose a process that could achieve this. (b) Can the proposed process be used to form large objects with complex shapes? Explain.

### Chapter 11, Solution 111

Place a Si substrate inside a chamber at high temperatures ( $\sim 600^\circ\text{C}$ ) and pressure of around 25 – 100 Pa. Expose the surface to nitrogen containing gas. Nitrogen will react with Si on its surface and form  $\text{Si}_3\text{N}_4$  which serves as an insulator. This process is called chemical vapor deposition (CVD). It would be difficult to apply this process (expensive) to very large objects because of the complexity of the process. Other approaches have to be used for larger objects and more commercial applications.

### Chapter 11, Problem 112

Explain, from an atomic structure point of view, why metals can be plastically deformed to form large and complex shapes while complex ceramic parts cannot be manufactured by this technique.

### Chapter 11, Solution 112

It is easy to form complex shapes from metals using processes such as casting (figure 6.2 c) and forging (figure 6.10). One can melt metals easily and cast them or plastically deform (slip) them into complex shapes. Because metals melt easily and deform due to movement of dislocation, little energy is needed to make complex parts from them. This is not the case with ceramics. Standard melting and casting techniques do not work with ceramics. That is why we use powder metallurgy to compact and sinter ceramic components. Also, it is practically impossible to cause dislocation movement in ceramics due to strong ionic/covalent bonds between atoms. In other words, it is very difficult to cause slip in ceramics (they simply fracture and not deform).

### Chapter 11, Problem 113

Alumina ( $\text{Al}_2\text{O}_3$ ) and chromium oxide ( $\text{Cr}_2\text{O}_3$ ) are ceramic materials that form an isomorphous phase diagram. (a) What does this tell you about the solubility limit of one component in the other? (b) What type of a solid solution is formed? (c) Explain what substitution takes place.

### Chapter 11, Solution 113

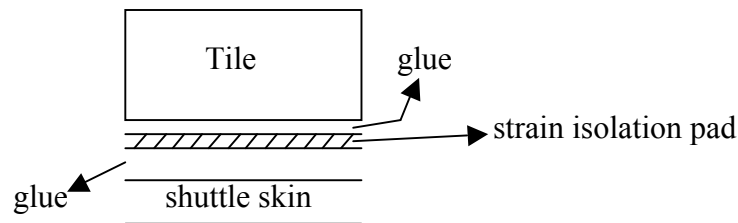
- a) Because the alloy system is isomorphous, there is unlimited solubility of one ceramic in the other. In other words, any combination of wt%  $\text{Al}_2\text{O}_3$  and  $\text{Cr}_2\text{O}_3$  is possible.
- b) The solid solution formed will be of the substitutional nature.
- c)  $\text{Cr}^{+++}$  will replace  $\text{Al}^{+++}$  and vice versa.

### Chapter 11, Problem 114

How are the ceramic tiles used in the thermal protection system of the space shuttle attached to its frame? (b) Why is the thermal protection system of the space shuttle made from small tiles (15 to 20 cm width) and not larger, more contoured ones?

### Chapter 11, Solution 114

- a) Because the space shuttle tiles are made of ceramics (silica fibers), and because ceramics are brittle, they cannot be connected to the frame via fasteners (holes cannot be drilled in tiles) or welded (impractical). Thus, the best approach is to glue the tiles to the frame using silicon adhesive. A strain isolation pad is placed between the tile and the shuttle skin (aluminum alloy).



- b) Because it is very difficult to manufacture a complex one piece underbelly of the shuttle from ceramics. Such manufacturing process is very challenging. Secondly, due to brittle nature of the ceramic, it is structurally unwise to have a one-piece underbelly. If the body fractures, it will cause catastrophic fracture of the whole underbelly. With smaller pieces however, any cracks will be contained in that piece alone.

### Chapter 11, Problem 115

The nose cap and the wing leading edges of the space shuttle may reach temperatures of up to 1650°C. (a) Would the silica fiber compound (HRSI) be a suitable candidate for these sections of the shuttle? (b) If not, select a suitable material for this location. (c) Investigate the important properties of the selected material that satisfy the design needs.

### Chapter 11, Solution 115

- a) The HRSI would not be suitable because it can only withstand  $\sim 1260^\circ\text{C}$ , far short of  $1650^\circ\text{C}$ .  
b) For the appropriate material refer to the chapter opener of chapter 12. Carbon-carbon composites can maintain their integrity in temperatures as high as  $2800^\circ\text{C}$ .  
c) The most critical issue is for the material to withstand thermal shock (a sudden increase in temperature). It must also have high thermal conductivity.

### **Chapter 11, Problem 116**

Carbon/carbon composites have desirable properties at very high temperatures that make suitable materials for many aerospace applications. However, the carbon in the material can react with the oxygen in the atmosphere at temperatures above 450°C, and gaseous oxides form. Develop solutions for this problem.

### **Chapter 11, Solution 116**

To avoid reaction with oxygen above 450°C, the material should be coated or converted to a temperature resistant coating such as SiC. A complex process is applied to coat the top surface with SiC and this protects the carbon-carbon composite from reacting with oxygen.

### **Chapter 11, Problem 117**

Low toughness is the major problem for many structural ceramics. Many cutting tools are made of ceramics with improved toughness. For example, tungsten carbide particles (WC) are embedded in a metal matrix such as nickel or cobalt. (a) Explain how this improves the toughness of the tool. (b) How is the choice of matrix material important (i.e., would aluminum work as the matrix material)?

### **Chapter 11, Solution 117**

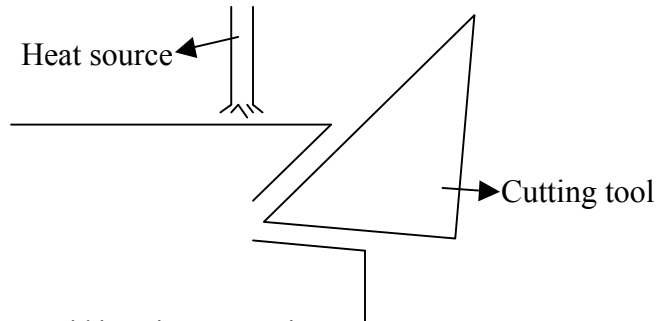
By mixing tungsten carbide particles with a metal matrix, a metal-ceramic composite material is produced. The composite will have improved toughness due to the high toughness of the matrix (nickel or cobalt). The composite will also have improved strength and hardness due to the strength of tungsten carbide. It is important that the matrix material also have a high melting or thermal softening temperature. Thus, aluminum would not work due to its low melt temperature.

### **Chapter 11, Problem 118**

It is very difficult to machine ceramic components to a desired shape. This is because ceramics are strong and brittle. The stresses produced due to cutting forces could create surface cracks and other damages that, in turn, weaken the component. Propose a technique that will reduce the cutting forces and the possibility of cracking during machining of ceramics.

### Chapter 11, Solution 118

It is possible to machine a ceramic without extensive damage by heating the part ahead of the cutting tool to very high temperatures. For instance, the strength of alumina drops significantly, around 1000°C.



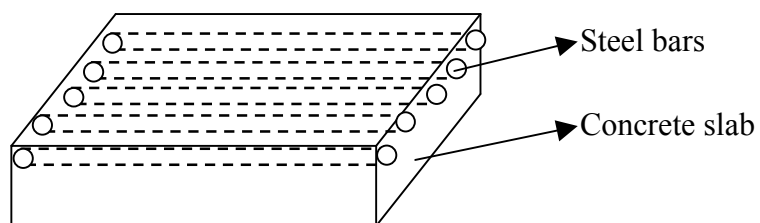
The heat source could be a laser or a plasma source.

### Chapter 11, Problem 119

Concrete is an important construction material that is classified as a ceramic (or a ceramic composite) material. It has excellent strength characteristics in compression but is extremely weak in tension. (a) Propose ways of improving the tension bearing characteristics of concrete. (b) What problems do you anticipate in your process?

### Chapter 11, Solution 119

- a) The strength of concrete can be improved in tension by placing steel bars/rods inside the concrete.



For instance, in the above schematic, if the top surface of the slab is exposed to tension due to bending, the steel bars will support the tension and will protect the concrete slab from fracture and failure.

- b) The bonding between concrete and steel bars must be adequate. If the bonding is not adequate, the tensile load will not be transferred to the bars, and the slab will crack.



### Chapter 11, Problem 120

Refer to Fig. 11.48, in which glass plates are strengthened by inducing compressive stresses on the surfaces. Suggest a way of producing compressive stress on the surfaces of a concrete slab using mechanical means. Show schematically how this will help.

### Chapter 11, Solution 120

It is possible to induce compressive stresses on the surface of the concrete using mechanical means:

1. Place steel bars at the bottom of the cast
2. Apply tension to the steel bars (axial tension) and maintain
3. Pour concrete into the cast
4. After settling in, remove the tensile load from the bars
5. As the tensile load is removed, the steel bars want to return to the original length and this puts the surface in compression.

### Chapter 11, Problem 121

Conventional taps are prone to dripping because rubber washers are susceptible to wear and the metal seat (brass) is susceptible to pitting corrosion. (a) Which class of materials would be a suitable replacement for the rubber/metal combination that would reduce the dripping problem? (b) Select a specific material for this problem. (c) What problems would you anticipate in using or manufacturing of these components?

### Chapter 11, Solution 121

- a) Clearly, ceramics resistance to pitting corrosion and wear makes them excellent candidates for this application.
- b) Alumina ( $\text{Al}_2\text{O}_3$ ) would be an excellent candidate due to its wear resistance.
- c) Cost would be an issue. As such parts may be hard to manufacture at a high rate.

### Chapter 11, Problem 122

A major problem in the selection of ceramic materials for various applications is the thermal shock (rapid temperature change similar to during re-entry or breaking) resistance. (a) What factors control thermal shock resistance of a material? (b) What specific ceramics have the best thermal shock resistance?

### Chapter 11, Solution 122

- a) The most important factor is the ability of the material to conduct heat rapidly. If not, temperature will increase locally and cause damage.

The second factor is low coefficient of thermal expansion. High thermal expansion could cause severe thermo-mechanical stresses leading to damage in the material.

b) HRSI and carbon-carbon ceramics have excellent thermal shock properties.

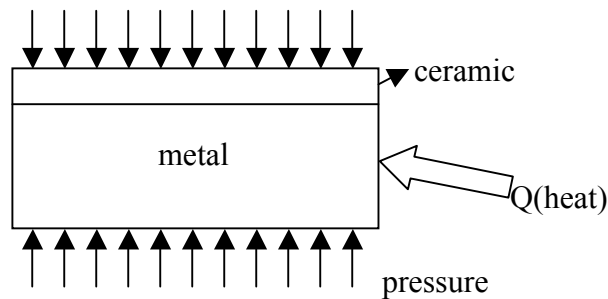
### Chapter 11, Problem 123

Give examples of applications in which a ceramic material must join a metal. How would you join a ceramic to a metal?

### Chapter 11, Solution 123

In the engine environment, often it is necessary to coat the surface of the piston or the cylinder with a ceramic material to protect the metal against high temperature oxidation and corrosion.

A ceramic coating can be produced on a metal substrate using simultaneous application of pressure and heat. Refer to the opener for chapter 5 for details.



### Chapter 11, Problem 124

(a) In selecting the material for the windshield of automobiles, what type of glass would you use? (b) Propose a process that would keep glass shards from dispersing if the glass fractures.

### Chapter 11, Solution 124

- Clearly for auto applications, one must use the strongest glass. Tempered glass is an excellent candidate due to the compressive residual stresses on its surfaces. An applied tensile load must first overcome the compressive stresses in glass, before it can cause any damage.
- One can use a thin transparent polymer sandwiched between two layers of tempered glass. The adhesive forces between the glass and the polymer will not allow the fractured pieces to fly away and cause additional damage.

### **Chapter 11, Problem 125**

In what coating applications would you choose ceramic coating as opposed to metallic or polymeric coating? Why? Give specific examples.

### **Chapter 11, Solution 125**

Ceramic coatings are better suited for high temperature applications protecting against corrosion. Metallic and polymer coatings are more suitable for low temperature applications due to lower cost.

Example for ceramic coating: engine environment

Example for metal coating: galvanized steel

Example for polymer coating: boat glaze

### **Chapter 11, Problem 126**

Oxide coatings are usually used to protect against oxidation and damage at elevated temperatures, and carbides are used to protect against wear. Can you explain why? Give examples.

### **Chapter 11, Solution 126**

Carbides are generally much harder than oxides and do better for protection against wear.

Example: Zirconia on aluminum to protect against oxidation.

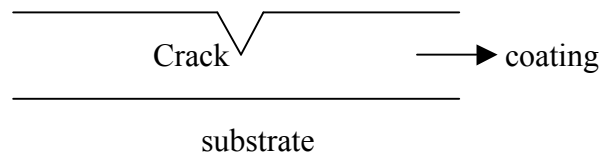
Tungsten carbide on steel rollers to protect against wear.

### Chapter 11, Problem 127

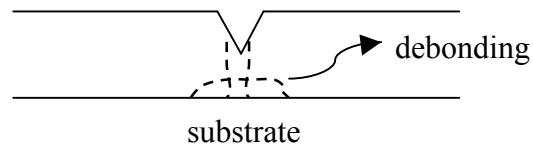
During inspection a small crack is found in the ceramic coating of a component. Would you be concerned about this small crack?

### Chapter 11, Solution 127

If the application is non-stress bearing and if the crack has not reached the substrate, then there is no immediate concern. The substrate is still protected.



If the application is load bearing, then there is a cause for concern because the crack could grow and cause debonding. This will expose the substrate to damage. The coating must be repaired.

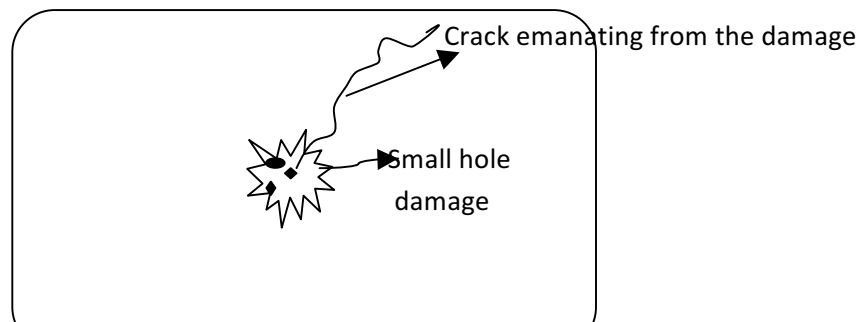


### Chapter 11, Problem 128

Due to impact of hail, there is a very small circular damage to the surface of your automobile windshield. (a) What happens if you ignore this small damage? (b) How would you fix this without changing the windshield?

### Chapter 11, Solution 128

- a) If the damage is ignored, large cracks will emanate from these regions. This will result in changing of the windshield.



Cyclic loading will cause the crack to grow bigger until it covers the full windshield

- b) The common approach is to fill the damaged area with epoxy (glue) under pressure. The epoxy fills the voids produced due to hole and will practically stop growth and propagation of cracks.

### Chapter 11, Problem 129

If there is a 1-in. crack in your automobile windshield and you would like to slow down its propagation, what would you do?

### Chapter 11, Solution 129

The best approach is to dull the crack tip with a sharp object. This will reduce the stress-concentration effect and slows down the propagation of the crack.

