32

Interacting with and Generating Light

CHAPTER PREVIEW

In this chapter we examine four key properties of ceramic materials all of which we can classify as *optical*. (1) Ceramics can be transparent, translucent, or opaque for one particular composition. (2) The color of many ceramics can be changed by small additions: additives, dopants, or point defects. (3) Ceramics can emit light in response to an electric field or illumination by light of another wavelength. (4) Ceramics can reflect and/or refract light. We will discuss why these effects are special for ceramics and how we make use of them.

The optical properties of ceramics result in some of their most important applications. In their pure form, most dielectric single crystals and glasses are transparent to visible light. This behavior is very different from that of metals and semiconductors, which, unless they are very thin (<1 μm), are opaque. Many ceramics and glasses also show good transparency to infrared (IR) radiation. This property has led to the use of glasses for optical fibers for high-speed communications.

We can produce polycrystalline ceramics that are highly transparent. The ability to make translucent and transparent polycrystalline ceramics was developed in the 1960s when it was discovered that small additions of MgO to Al_2O_3 powder could produce a fully dense ceramic by sintering. This product is widely used in streetlights (the golden glow).

If a transparent ceramic or glass is doped, for example, by the addition of transition metal ions, the material becomes colored. We will discuss the different types of colors that can be produced in ceramics. The doping of Al_2O_3 with Cr^{3+} produces ruby, which is used as an optical cavity in a solid-state laser. The ruby laser was the first solid-state laser. There are now many more examples of solid-state lasers using colored ceramics and glasses as the optical cavity. We will describe how solid-state lasers work and the different wavelengths of radiation that can be produced. Phosphors produce light as a result of excitation by, e.g., electron irradiation. Again, we are using doped ceramics for this application because, as we will see, doping changes the electronic band structure of the ceramic.

32.1 SOME BACKGROUND FOR OPTICAL CERAMICS

Electromagnetic Spectrum, the Terminology and Units

Table 32.1 lists some of the major terms, and their units, that we will encounter in this chapter. It also lists the important physical constants that are needed to describe the optical properties of materials. The electromagnetic spectrum embraces a wide range of wavelengths, from the very short γ rays to the long radio waves.

The portion of the spectrum that the human eye can detect is quite small. To put this in context, the full electromagnetic spectrum is shown in Figure 32.1. Radiation with a single wavelength is referred to as monochromatic; λ and *f* are related through *c*:

$$f = \frac{c}{\lambda} \tag{32.1}$$

The frequency never changes regardless of the density of the medium through which the monochromatic light passes; however, the velocity of propagation and λ do change. For a high-density medium, such as glass, the velocity is lower than it would be in a vacuum and, consequently, λ is proportionally smaller. (A dense medium has a lower *c*.) The light waves are retarded because of the interaction of the electro-

λ AND COLOR

Ultraviolet (UV) is short λ
Blue is 390 nm
Green is 550 nm
Red is 770 nm
IR is long λ

TABLE 32.1 Terms and Units Used in Optics

Parameter	*Definition*	*Units/value*	*Conversion factor*
λ	Wavelength	m	1 Å = 10^{-10} m
f	Frequency	Hz	
v	Velocity	m/s	
n	Refractive index	Dimensionless	
Δn	Birefringence	Dimensionless	
c	Speed of light	2.998×10^8 m/s	
R	Reflected light	Dimensionless	Ratio given by Eq. 32.6
T	Transmitted light	Dimensionless	Ratio given by Eq. 32.2
E_g	Band gap energy	eV	1 eV = 0.1602 aJ
I	Intensity	cd	
ε_0	Permittivity of a vacuum	8.85×10^{-12} F/m	See also Section 31.1
R_∞	Molar refractivity		Directly proportional to electronic polarizability (see Section 31.1)
N_o	Avogadro's number	6.022×10^{23} mol^{-1}	
r_c	Linear electrooptic coefficient	m/V	
R	Quadratic electrooptic coefficient	m^2/V^2	
P	Polarization	C/m^2	See also Section 31.1
E_c	Coercive field	V/m	

magnetic radiation and the electrons of the atoms that make up the material.

The Nature of Light

Maxwell's equations describe how an electromagnetic wave originates from an accelerating charge and propagates in free space with a speed of 2.998×10^8 m/s. An electromagnetic wave in the visible part of the spectrum may be emitted when an electron changes its position relative to the rest of an atom, involving a change in dipole moment. Light can also be emitted from a single charge moving at high speed under the influence of a magnetic field: because the charge follows a curved trajectory it is accelerating and, as a consequence, radiating. (The same principle is used to produce high-energy X-rays at a synchrotron.)

An electromagnetic wave in free space comprises an electric field **E** and a magnetic induction field **B** that lie in mutually perpendicular directions in a plane normal to the wave propagation direction as shown in Figure 32.2. Remember that a dielectric material reacts to electromagnetic radiation because the opposite electrical charges are displaced in opposite directions; this dielectric property is the underlying reason for refraction and absorption in glass.

Absorption and Transmission

The classical description of the absorption of electromagnetic radiation by materials indicates that it occurs by two basic mechanisms:

- *Electronic transitions*: electrons are excited from the valence band into unfilled energy states in the conduction band.
- *Absorption*: the light excites vibrational and rotational vibrating modes in the dielectric material since it is associated with an oscillating electric field.

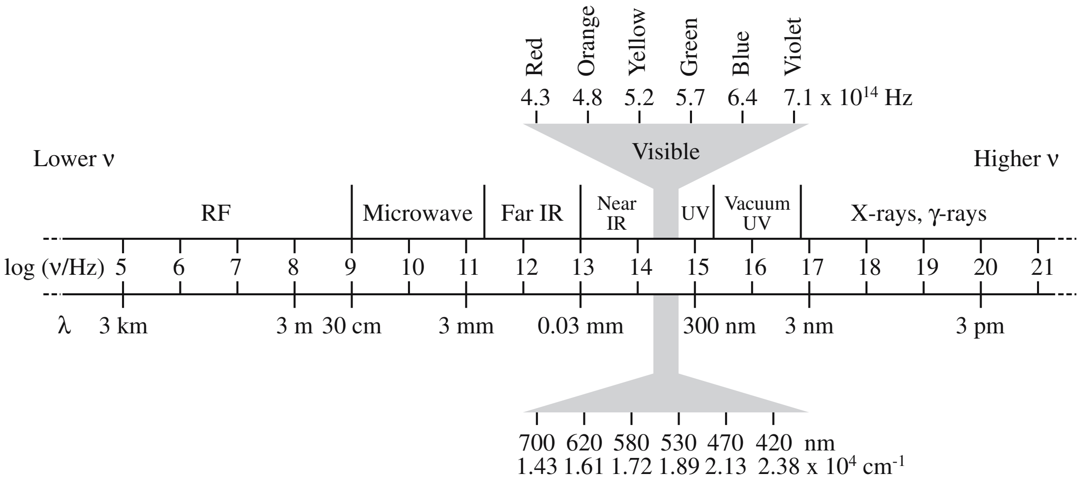

FIGURE 32.1 The electromagnetic spectrum. The visible region has been expanded for clarity. It is actually a very small part of the spectrum.

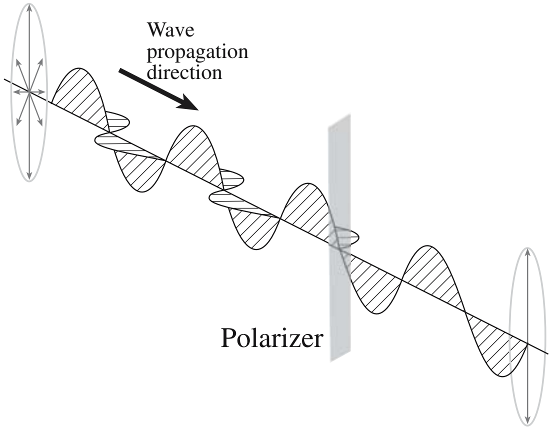

FIGURE 32.2 Polarization of light.

For a single-phase material we can express the fraction of light transmitted, T, as

$$T = I/I_0 = \exp(-\beta x) \qquad (32.2)$$

where I is the transmitted intensity, I_0 is the intensity of the incident light, x is the optical path length (the thickness as seen by the light beam), and β is the absorption coefficient. Equation 32.2 is a mathematical representation of Lambert's law, which simply states that the fraction of light that is transmitted by a material does not depend on the intensity of the incident light. The parameter β varies with λ; this variation is important because it causes color when light is transmitted. If the absorption is due to a particular dopant ion then Eq. 32.2 is modified by setting β equal to εC; C is the concentration of the absorbing ion and ε is the absorption per unit concentration. This is the Beer–Lambert law. In real life, we also have scattering by defects in the bulk or at the surface.

Ultraviolet absorption corresponds to electronic transitions from the filled valence band to the unfilled conduction band: the larger E_g is, the greater the range of transparency in the UV. Infrared absorption occurs by elastic vibrations.

Refraction

Refraction is the phenomenon that is responsible for making lenses work. The ratio of the velocity of light in a vacuum to that in any other medium is known as the refractive index, n. Expressed mathematically, n is given by the simple equation

$$n = \frac{c}{c_m} \qquad (32.3)$$

where c_m is the velocity of light in the material (the medium). Since c_m is always less than c, values of n are always greater than unity and range from 1.0003 (air) to approximately 3.0 for very dense solids. Clearly n is not a constant for any ceramic, since it depends on c_m; n is a function of λ. The variation of n with λ produces a dispersion of the light:

$$\text{Dispersion} = dn/d\lambda \qquad (32.4)$$

The ability of a substance to refract or "bend" light waves is sometimes described as refringence. Crystals having one unique axis (optic axis) along which the index of refraction is different from the index along the other orthogonal axes are known as uniaxial birefringent crystals. The magnitude of the difference between the two indices of refraction is referred to as the birefringence, or simply, Δn. It is defined as

$$\Delta n = n_e - n_o \qquad (32.5)$$

where n_e is the index of refraction of a light wave vibrating in a plane parallel to the optic axis but traveling in a direction perpendicular to the optic axis, n_o is the index of refraction of a wave vibrating parallel to either of the other axes and traveling in the direction of the optic axis, o is the ordinary ray, and e is the extraordinary ray. The value of the birefringence may be positive or negative. Glass cannot be birefringent because it is isotropic. Ceramics from all noncubic crystal systems do show birefringence.

Ceramic applications of refraction are numerous: from the glass spheres used in road signs to the sparkle in diamonds. The trilobite eye made use of refraction in calcite (Section 32.16).

Reflection

The amount of light reflected from a surface of a material in air is determined by the refractive index of the reflecting medium. At normal incidence, the fraction, R, of light reflected (in medium 1) from the interface between two dielectric materials (1 and 2) is given by Fresnel's equation:

$$R = (n_2 - n_1)^2/(n_2 + n_1)^2 \qquad (32.6)$$

For air ($n_1 \sim 1$) and "optical" glass ($n_2 \sim 1.5$) R is ~4%, whereas lead-crystal glass ($n_2 \sim 2.1$) gives an R of ~13%. Equation 32.6 will be very important when we use dielectrics as antireflection coatings (ARCs); we then have to consider two interfaces. The thickness of the films and the nature of the reflecting surface will also be important. Ceramic applications of reflection are numerous but are often linked to refraction.

32.2 TRANSPARENCY

Dielectrics generally show good transmission in the visible part of the electromagnetic spectrum as shown in Figure 32.3. In the UV, absorption corresponds to electronic transitions from the filled valence band to the unfilled

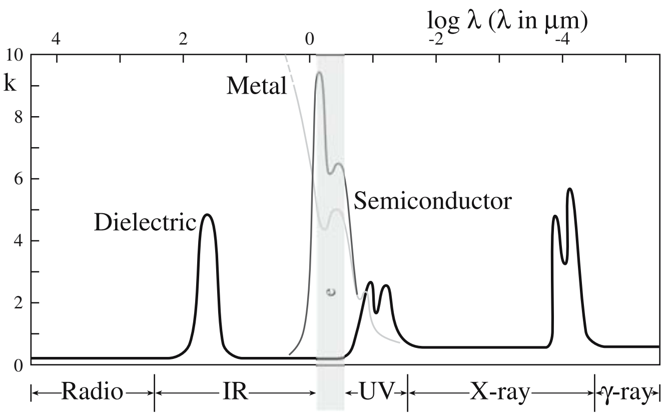

FIGURE 32.3 Comparison of the frequency variation of absorption for metals, semiconductors, and dielectrics. The visible region of the spectrum is shaded.

conduction band. Ceramics with large values of E_g are transparent to shorter UV wavelengths. In the IR, absorption by elastic vibrations is the result of loss of transparency. This absorption occurs at longer wavelengths for materials that contain large ions held together by weak interatomic forces: large ions and weak bonds lead to low frequencies, i.e., small f, which implies large λ, i.e., long wavelength. Transparency in the microwave and radio frequency (RF) region is critical for radomes that house the guidance system on missiles. Ceramics are the only materials that are suitable for this application.

32.3 REFRACTIVE INDEX

Refraction is the bending of a beam of light when it enters a dielectric. The physical reason for this is that the velocity of light is different inside the dielectric. We are used to this happening in water or glass but in crystals the situation can be more complex when crystals are anisotropic. The classic example is calcite, which is illustrated in Figure 32.4.

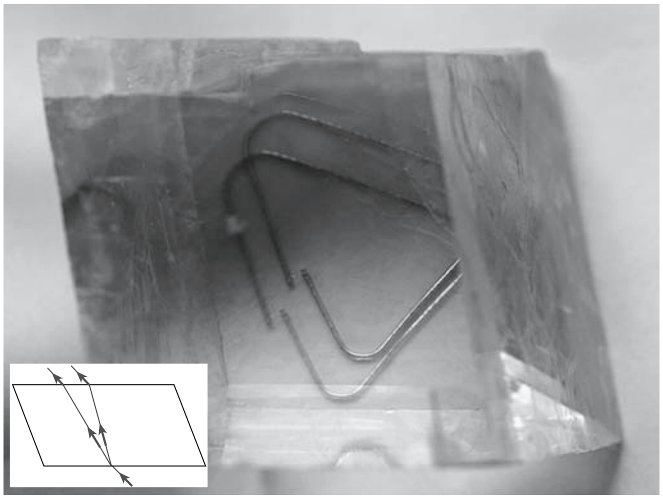

FIGURE 32.4 Birefringence in calcite: two images of one paperclip.

The refractive index of several ceramic materials is given in Table 32.2. We have seen that the value of n is a function of λ. It normally decreases as λ increases and this trend is illustrated for a range of ceramics in Figure 32.5. The reason for this behavior is that colorless solids and glasses have characteristic frequencies in the UV where they become opaque. For example, the important characteristic frequencies for glasses occur at $\lambda \approx 100\,\text{nm}$. The dispersion as a function of λ for several ceramics is shown in Figure 32.6. Dispersion is important in creating "fire" in gemstones (see Chapter 36). Several factors influence n.

- *Ion size.* Materials containing large ions have large values of n because large ions are more easily polarized than small ions. The Lorentz–Lorentz equation quantifies the relationship between polarizability, α, and n.

TABLE 32.2 Refractive Indices of Some Glasses and Crystals

	Average refractive index	*Birefringence*
Glass composition		
From orthoclase ($KAlSi_3O_8$)	1.51	
From albite ($NaAlSi_3O_8$)	1.49	
From nepheline syenite	1.50	
Silica glass, SiO_2	1.458	
Vycor glass (96% SiO_2)	1.458	
Soda-lime–silica glass	1.51–1.52	
Borosilicate (Pyrex) glass	1.47	
Dense flint optical glasses	1.6–1.7	
Arsenic trisulfide glass, As_2S_3	2.66	
Crystals		
Silicon chloride, SiCl4	1.412	
Lithium fluoride, LiF	1.392	
Sodium fluoride, NaF	1.326	
Calcium fluoride, CaF_2	1.434	
Corundum, Al_2O_3	1.76	0.008
Periclase, MgO	1.74	
Quartz, SiO_2	1.55	0.009
Spinel, $MgAl_2O_4$	1.72	
Zircon, $ZrSiO_4$	1.95	0.055
Orthoclase, $KAlSi_3O_8$	1.525	0.007
Albite, $NaAlSi_3O_8$	1.529	0.008
Anorthite, $CaAl_2Si_2O_8$	1.585	0.008
Sillimanite, $Al_2O_3 \cdot SiO_2$	1.65	0.021
Mullite, $3Al_2O_3 \cdot 2SiO_2$	1.64	0.010
Rutile, TiO_2	2.71	0.287
Silicon carbide, SiC	2.68	0.043
Litharge, PbO	2.61	
Galena, PbS	3.912	
Calcite, $CaCO_3$	1.65	0.17
Silicon, Si	3.49	
Cadmium telluride, CdTe	2.74	
Cadmium sulfide, CdS	2.50	
Strontium titanate, $SrTiO_3$	2.49	
Lithium niobate, $LiNbO_3$	2.31	
Yttrium oxide, Y_2O_3	1.92	
Zinc selenide, ZnSe	2.62	
Barium titanate, $BaTiO_3$	2.40	

$$\alpha = \frac{3\varepsilon_0}{N_0}\frac{n^2-1}{n^2+2}\frac{M}{\rho} = \frac{3\varepsilon_0}{N_0}R_\infty \tag{32.7}$$

where M is molar weight and ρ is density.

The refractive index of SiO_2 glass can be raised by adding GeO_2. This has important implications in the fabrication of optical fibers (Section 32.11).

- *Structure.* Less dense polymorphs of a particular material will have a more open structure and thus a lower n than their denser counterparts. We can illustrate this with the case of SiO_2, which can exist as a glass or in several crystallographic forms: $n_{\text{glass}} = 1.46$, $n_{\text{tridymite}} = 1.47$, $n_{\text{cristobalite}} = 1.49$, and $n_{\text{quartz}} = 1.55$.

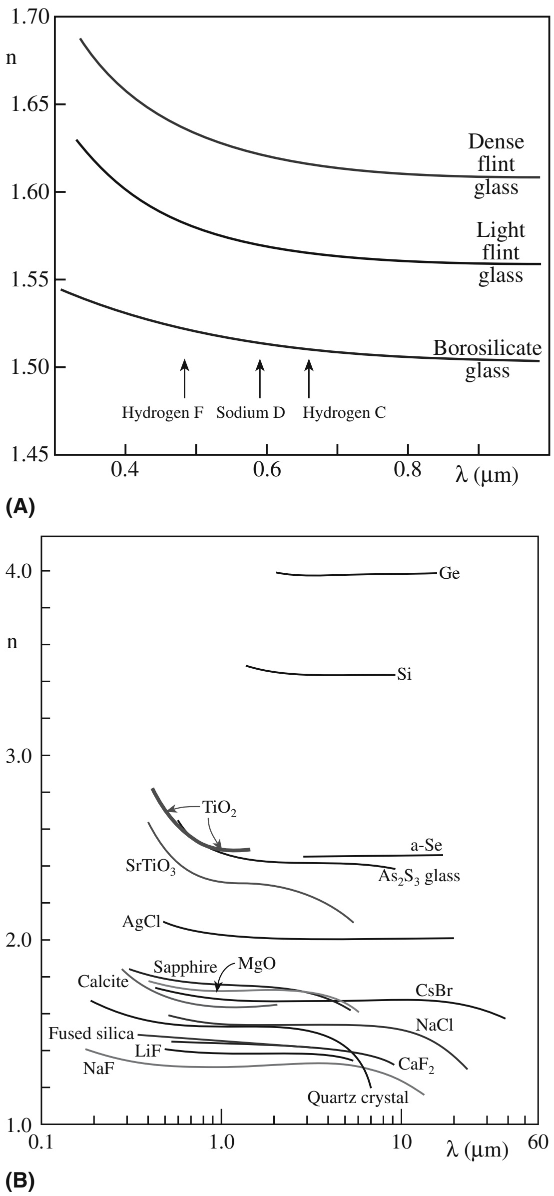

FIGURE 32.5 (a) Change in n with λ for several commercial glasses. (Hydrogen F, Sodium D, and Hydrogen C refer to specific light sources that have λ = 589, 486, and 656 nm, respectively.) (b) Change in n with λ for several ceramics and glasses.

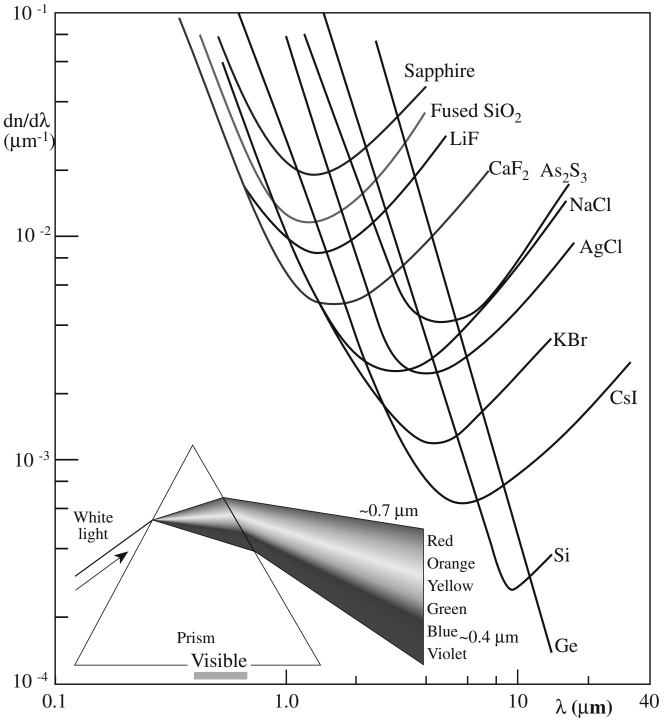

FIGURE 32.6 Dispersion as a function of wavelength for a number of ceramics. The inset is the classic illustration of dispersion, a prism separating white light into its spectral components.

- *Crystallographic direction.* Glasses and crystals with a cubic structure are optically isotropic. In all other crystal systems n is higher along close packed directions.
- *Stress.* The application of tensile stress to an isotropic material causes an increase in n normal to the direction of the applied stress and decreases n along the stressed direction. The situation is the exact opposite if a compressive stress is applied. The change of n with applied stress is known as stress birefringence.

32.4 REFLECTION FROM CERAMIC SURFACES

Using Eq. 32.6 we can determine the reflectivity from the surface of various ceramics and glasses. The reflectivity is about 4% from a surface with $n = 1.5$ and about 10% for a surface with $n = 1.9$. A high reflectivity is often important for aesthetic reasons. The high reflectivity, $R = 13\%$, of lead "crystal" glass, glass that contains a high amount of PbO, is due to its high refractive index, $n = 2.1$. The reflectivity is more than twice that of normal silicate glasses. High reflectivity is important for gemstones, where it affects the brightness and sparkle of the stone. This is partly the result of the cutting skills of the jeweler and the fact that gemstones have high values of n. The refractive index of diamond is 2.4.

High reflectivity for glazes and enamels is also important, and can be achieved by using glass formulations with

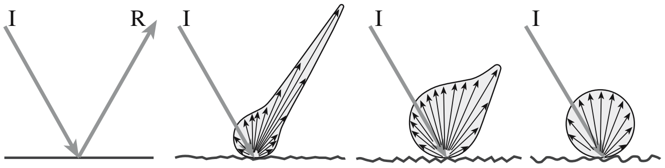

FIGURE 32.7 Effect of surface roughness on reflectivity. I, incident; R, reflected.

a high PbO content. However, it is important to test the formulation carefully to make sure that high concentrations of Pb do not leach out into food and beverage items. (Hence there is a protocol for the leach-testing of glazes; see Section 2.5).

The reflectivity of a glaze or enamel is reduced if the surface is rough. Roughness causes considerable diffuse reflection from the surface as illustrated in Figure 32.7.

- Specular reflection is light reflected at a single angle (conventional reflection).
- Diffuse reflection occurs when light is reflected through a range of different angles.

In some situations we do not want a high reflectivity. In fact, we want to minimize the reflectivity as far as possible. One very effective way of reducing the reflectivity of a glass surface is to coat it with an antireflection (AR) coating (giving an ARC). A good ARC can cut the percentage of light reflected from >5% to <0.2%. One example is the purple colored ARC on binocular and camera lens. Catalogs for optical equipment will often indicate whether the lens has an ARC applied. The principle behind how an ARCs works is illustrated in Figure 32.8. The coating is applied onto the glass surface so that its thickness is one-quarter of the wavelength of the incident light. For an ARC optimized for green light ($\lambda = 530\,\text{nm}$), which is in the center of the electromagnetic spectrum (and where the eye is most sensitive), the thickness of the ARC should be about 130 nm (0.13 μm). Light reflected from the top surface of the coating is exactly out of phase with light reflected from the glass surface, and so there is destructive interference and no net reflected beam. Magnesium fluoride (MgF_2) is a widely used ARC material and is usually applied onto the glass surface by a physical vapor deposition (PVD) process such as evaporation. A single layer of MgF_2 ($d = \lambda/4$) will reduce the reflectance of glass from about 4% to a little more than 1% over the visible spectrum. Antireflective coatings are also applied to glass for architectural applications to help with radiation control (see Section 26.7).

A LIGAND

A ligand is any molecule or ion that is bonded to a metal ion.

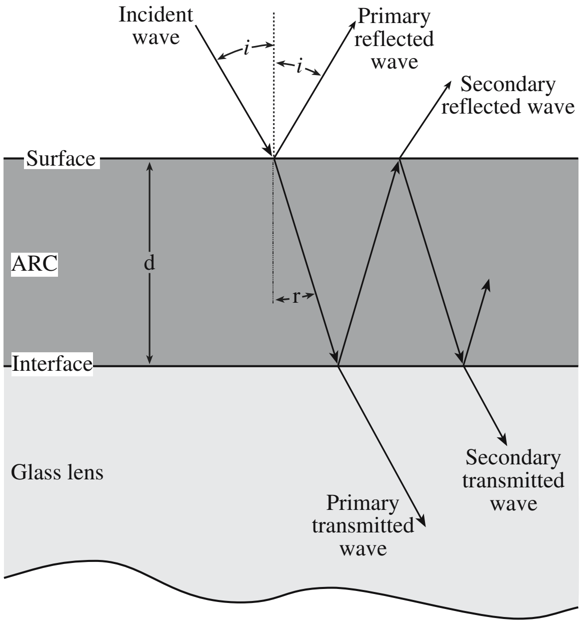

FIGURE 32.8 Illustration of how an ARC works.

32.5 COLOR IN CERAMICS

We discussed colorants in history throughout Chapter 2, F centers in crystals in Section 11.9, and the origins of color in glass in Section 21.8; we will discuss color more in Chapter 36.

Most dielectric ceramics and glasses are colorless because of their large E_g. They become colored when energy states are added within the band gap. These new levels allow electron transitions to occur within the visible part of the electromagnetic spectrum.

The most common way to color a ceramic is by adding transition metals (TM), particularly Ti, V, Cr, Mn, Fe, Co, and Ni, where the 3d is partly filled.

To explain how the addition of a TM to a colorless ceramic makes it colored we use the ligand field theory. In ceramics the most common ligand is oxygen, the O^{2-} ion. To understand the behavior of a transition metal once it is placed in a ligand field we need to consider the shapes of the d orbitals (see Figure 3.2). There are five of them and they are designated d_{xy}, d_{xz}, d_{yz}, $d_{x^2-y^2}$, and d_{z^2}. In a free ion, all the d orbitals are degenerate (i.e., they have the same energy). However, when the ion is put into a crystal the energy of the d orbitals is affected by the ligands.

Consider the case of the Ti^{3+} ion, which contains only a single 3d electron. If the Ti^{3+} ion is in an octahedral site (i.e., it is surrounded by six anions arranged at the corners of an octahedron) the energy of the $d_{x^2-y^2}$ and d_{z^2} orbitals is raised relative to the free Ti^{3+} ion because of repulsion from the surrounding anions. The energy of the other three orbitals is lowered, as illustrated in Figure 32.9a. If the Ti^{3+} ion were placed in a tetrahedral site (i.e., it is surrounded by four anions arranged at the corners of a tetrahedron), the energy of the $d_{x^2-y^2}$ and d_{z^2} orbitals is lowered with respect to the d_{xy}, d_{xz}, and d_{yz} orbitals. The total splitting for d orbitals is in the range of 1–2 eV, being lower

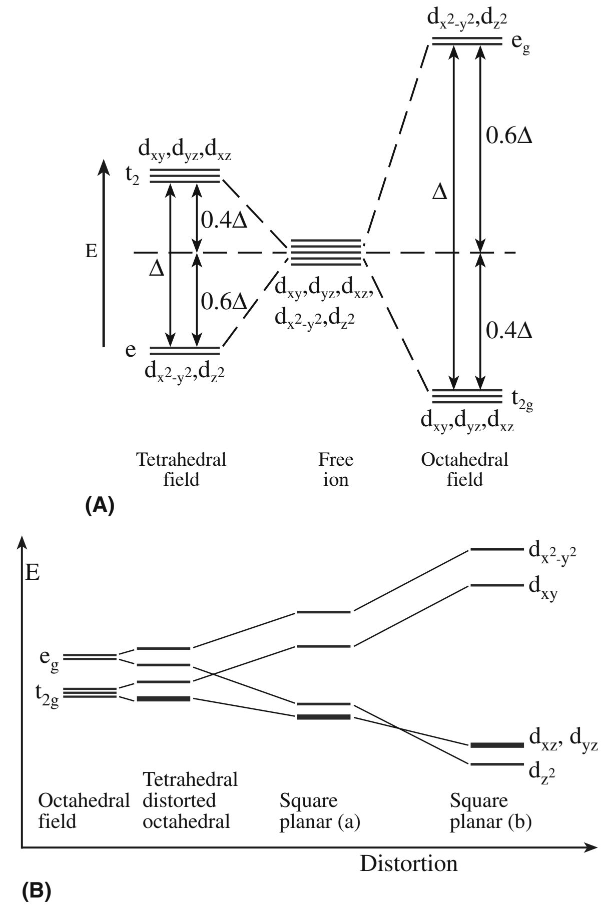

FIGURE 32.9 (a) Splitting of the d orbitals in a ligand field. (b) Splitting of d orbitals in a distorted octahedral ligand field in corundum.

for a tetrahedral ligand field than for an octahedral field. Hence absorption of light, associated with electronic transitions between the lower and upper d levels, generally occurs in the visible or near IR regions of the spectrum.

The situation is actually a little more complicated if we consider corundum, because the octahedral sites are slightly distorted. This distortion produces further splitting of the energy levels as illustrated in Figure 32.9b.

We can use a similar argument to show how the addition of rare earth (RE) elements, with incomplete f shells, also causes color. Table 32.3 shows the colors produced by the addition of RE ions to oxide glasses. Rare earth ions tend to color glass less strongly than do transition metal ions and the spectra usually consist of a large number of weak bands.

TABLE 32.3 Optical Absorption of Rare Earth Ions in Oxide Glasses

Ion	*Number of f electrons*	*Color*
Ce^{3+}	1	Green
Pr^{3+}	2	Green
Nd^{3+}	4	Violet
Sm^{2+}	6	Green
Eu^{2+}	7	Brown
Dy^{2+}	10	Brown
Ho^{3+}	10	Yellow
Er^{3+}	11	Pink

Other sources of color in ceramics include the following:

- F centers in alkali halides, which result from heating in alkali vapor. An F center in metal halides consists of a halide ion vacancy that has trapped an electron. This process creates additional energy levels between the valence band and the conduction band. A similar situation is found in MgO heated in Mg vapor: the F center consists of two electrons trapped at an oxygen vacancy. F centers are one example of so-called color centers. There are other types of possible color centers in ionic materials involving electrons and holes. (See Section 11.9; F is Farben.)
- Defects produced by X-ray or neutron bombardment. Irradiation of colorless quartz crystals with X-rays will result in the formation of a dark brownish gray to black color of "smoky quartz." Coloration is due to the formation of a color center, a hole color center this time. If the smoky quartz is heated to several hundred °C it will become clear again.
- Defect states produced as a result of nonstoichiometry. This occurs in, e.g., TiO_2 and ZrO_2.

32.6 COLORING GLASS AND GLAZES

To color glass, TM oxides or RE oxides are added to the glass batch. Color is produced through selective light absorption by the TM or RE ion, which is incorporated into the glass structure. The mechanism essentially uses a solution approach to coloring. The color results when the absorbing ion removes light of certain wavelengths, so we see the complementary color in transmission.

Uses for colored glass include not only the obvious stained glass windows and Tiffany lampshades but also the glazes used to seal and decorate cups and pots. Adding Pb to make X-ray-absorbing glass is essentially the same process/motivation: the intent is to absorb the X-rays.

32.7 CERAMIC PIGMENTS AND STAINS

We color ceramics using inorganic pigments and stains that are relatively insoluble in the ceramic they are coloring; they should also be unaffected chemically and physically. This is not the same approach used for glass.

Table 32.4 shows the types of environment and temperatures that ceramic pigments must withstand. The colorant may be mixed directly with the ceramic body (this is called a body stain). An example is the coloring of

TABLE 32.4 Ceramic Environments for Colors

T *(°C)*	*Environment*	*Colorant type*	*Use*
700–900	Molten leaded/unleaded borosilicate glass	Enamel or overglaze colors	Tableware, tile decoration
900–1000	Molten lead/unleaded borosilicate or alkali borosilicate glasses	Low-temperature glaze stains, underglaze colors, colored pellets and granules	Tableware, wall and floor tiles
950–1200	Siliceous bodies	Body stains, brick surface colorants, colored pellets and granules	Tableware, floor tiles, fancies, bricks
1100–1350	Molten alkali/lime glasses	Glaze stains	Tableware, tiles, sanitary ware

house bricks—not all house bricks are the same color. If the stain is used to produce a glaze then actually we are coloring a glassy phase and coating the ceramic. An example of this approach is the glazing of sanitary ware and tiles (coloring whitewares). There are several classification systems for ceramic pigments. One of the most widely used is that drawn up by the Color Pigments Manufacturers Association (CPMA), formerly the Dry Color Manufacturers Association (DCMA), in the United States. This system provides a structural classification of pigments as summarized in Table 32.5. Fourteen classes of pigment and over 50 broad pigment subcategories cover all the principal mixed-metal oxide pigments manufactured today. However, it does not cover the full range of possible pigments. For example, nonoxide compounds, such as the Cd-based pigments, are not included.

PIGMENTS

Much of the information is covered in the patent literature. Zircon–vanadium blue was one of the most significant innovations in color technology for several decades. Seabright was also responsible for the praseodymium yellow and the zircon–iron coral pink.

In the CPMA classification, one commercially important class of pigments is the zircon pigments. Zircon is zirconium silicate, and the first patent for a zircon-based pigment was issued in the 1930s. Zircon pigments fall into two categories.

- Lattice type. The dopant ion replaces a Zr^{4+} ion in the zircon lattice, e.g., vanadium blue (V^{4+} replaces Zr^{4+}) and praseodymium yellow (Pr^{4+} replaces Zr^{4+}).
- Encapsulated type. Discrete particles of the colorant are trapped inside zircon crystals, e.g., the iron coral pink where very fine particles of red Fe_2O_3 are incorporated in zircon crystals.

TABLE 32.5 CPMA Classification of Mixed-Metal Oxide Inorganic Pigments

Pigment system, CPMA number	*Main components*	*Color*
I. Baddeleyite 1-01-4	Zr–V	Yellow
II. Borate 2-02-1	Co–Mg	Red-blue
III. Corundum-hematite 3-03-5	Cr–Al	Pink
IV. Garnet 4-07-3	Ca–Cr–Si	Green
V. Olivine 5-08-2	Co–Si	Blue
VI. Periclase 6-09-8	Co–Ni	Gray
VII. Phenacite 7-10-2	Co–Zn–Si	Blue
VIII. Phosphate 8-11-1	Co–Ni	Gray
IX. Priderite 9-13-4	Ni–Ba–Ti	Primrose
X. Pyrochlore 10-14-4	Pb–Sb	Yellow
XI. Rutile-cassiterite 11-15-4	Ni–Sb–Ti	Yellow
XII. Sphene 12-25-5	Cr–Sn–Si	Pink
XIII. Spinel 13-26-2	Co–Al	Blue
XIV. Zircon 14-42-2	Zr–Si–V	Blue

A different important class of pigments is the family of cadmium pigments. These are substitutional solid solutions between CdS and CdSe (both end members have the same crystal structure). Cadmium sulfide has a band gap $E_g = 2.6\,\text{eV}$. This provides absorption of violet and some blue but none of the other colors, leading to a yellow color. CdSe has $E_g = 1.6\,\text{eV}$ and is black. When CdSe is added to CdS the band gap of the material decreases and the color changes. This process is analogous to what we do in doping the III–Vs used to make light-emitting diodes (LEDs) in Section 32.12.

The achievable colors range from the yellow of CdS, through orange, to bright red and maroon as the percentage of CdSe is increased (Table 32.6). (The red is known

TABLE 32.6 Colors in the CdSe–CdS System

CdSe (mol%)	*CdS (mol%)*	*Color*
12.6	87.4	Orange
20.0	80.0	Orange-red
36.0	64.0	Light red
43.0	57.0	Dark red
49.0	51.0	Brown
54.5	45.5	Dark brown

as selenium ruby.) The red color is particularly significant because, for now, the only other additive that can produce the red color in glass is the metal Au. The stability of the selenide pigment is somewhat limited; it will oxidize at 650°C with a resultant loss of color. But if the pigment is encapsulated in a zircon matrix then it has the properties of zircon and is stable to at least 1300°C and is relatively inert in many environments.

A problem, of course, with Cd-containing pigments (like Pb in glass) is the toxicity of Cd. In some countries, e.g., Sweden, home of Orrefors and Kosta Boda, the use of Cd is prohibited. There is increasing pressure worldwide to reduce the use of potentially harmful or toxic species, such as Cd and Pb; there is therefore a growing need for developing suitable alternatives. Even if these additives can be managed during processing, it is difficult to control them during recycling; legislation can be aimed at the initial use (to protect the worker) or at recycling (e.g., so that heavy metals no longer enter the water supply).

32.8 TRANSLUCENT CERAMICS

Polycrystalline ceramics are often opaque, even though the single crystal may be transparent and E_g is large. We can also make glass that is not clear or is even opaque. The loss of transparency is due to scattering of the incident light, which can have several possible causes as illustrated in Figure 32.10.

- *Porosity.* The transmission decreases markedly with small increases in porosity as shown in Figure 32.11.

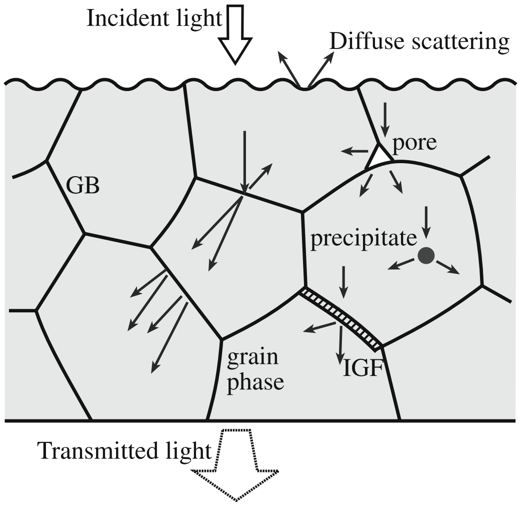

FIGURE 32.10 Mechanisms for loss of transparency due to scattering. GB, grain boundary; IGF, intergranular film. Details of the individual defects are described in Chapters 12–15.

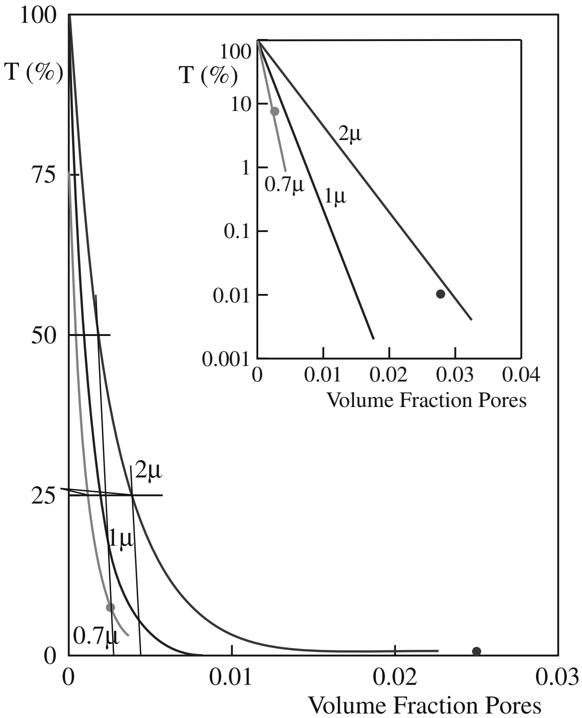

FIGURE 32.11 Effect of porosity on the transparency of polycrystalline alumina.

When the pore size is close to the λ of visible light then the scattering is maximized. This scattering can be engineered by controlling the sintering conditions or by hot pressing. Table 32.7 shows examples of processing conditions that have been shown to produce translucent ceramics.

- *Differences in n.* In general, light scattering can occur at grain boundaries (GBs) where refractive indices are discontinuous; this is especially easy for noncubic (i.e., anisotropic) structures. A similar situation can occur in multiphase materials, such as ceramics densified by liquid-phase sintering, where there may be an intergranular film (IGF). Matching refractive indices between different phases can reduce scattering losses. This approach is used in making high-quality bone china.
- *Grain size, r.* The effect of grain size on scattering is shown in Figure 32.12. Scattering is at a maximum when r is close to λ of visible light. For grain sizes smaller than the wavelength of the incident radiation, the scattering increases with r and is proportional to λ^{-4}. Scattering decreases rapidly as r increases and for large r it reaches a constant value.

The oldest glass objects in museums are opaque.

Frosted glass appears to be opaque because light is scattered at the surface.

TABLE 32.7 Sintering Additives and Conditions of Various Translucent Ceramics

Ceramic	*Sintering additive (wt%)*	*Transmissivity (%)*	*λ (μm) and specimen thickness (mm)*	*Sintering conditions*
Al_2O_3	MgO (0.25)	40–60	0.3 ~ 2 (1)	T = 1850–1900°C t = 16 hours Atmosphere: H_2
	Y_2O_3 (0.1), MgO (0.05)	70	0.3 ~ 1.1 (0.5)	T = 1700°C t = 5 hours Atmosphere: H_2
	MgO (0.05)	40	~0.9	T = 1700°C P = 0.06 Pa
	Y_2O_3, La_2O_3, ZrO_2 (0.1~0.5), MgO (0.55~1.0)	80	Visible light (~1)	T = 1700°C Atmosphere: H_2
	MgO (0.05)	85–90	Visible light (0.75)	T = 1725–1800°C t = 17–30 hours Atmosphere: H_2
CaO	CaF_2 (0.2~0.6)	40–70	0.4~8 (1.25)	T = 1200–1400°C t = 0.5–2 hours P = 0.5–0.8 GPa
MgO	LiF, NaF (1)	80–85	1~7 (5)	T = 1000°C t = 15 minutes P = 10 MPa *in vacuo*
	NaF (0.25)	Clear	Visible light	T = 1600°C t = 111 hours Atmosphere: O_2

32.9 LAMP ENVELOPES

An important application of transparent ceramics is found in the familiar high-intensity yellow streetlights that are common along major highways. These lamps are known as sodium-vapor lamps because during operation they contain sodium vapor that is being heated to a high temperature. Figure 32.13 shows the construction of a typical sodium-vapor lamp. The plasma temperature inside the lamp is 3700°C and the lamp envelope reaches a peak temperature of 1200°C; the Na vapor pressure is ~100 torr. The requirements for the envelope material are therefore very stringent: it has to be transparent to visible light, stable at high temperature, and must contain the corrosive Na plasma. It needs to be inexpensive because about 16 million units are made each year. The sodium-vapor lamp was made possible by the development of very dense

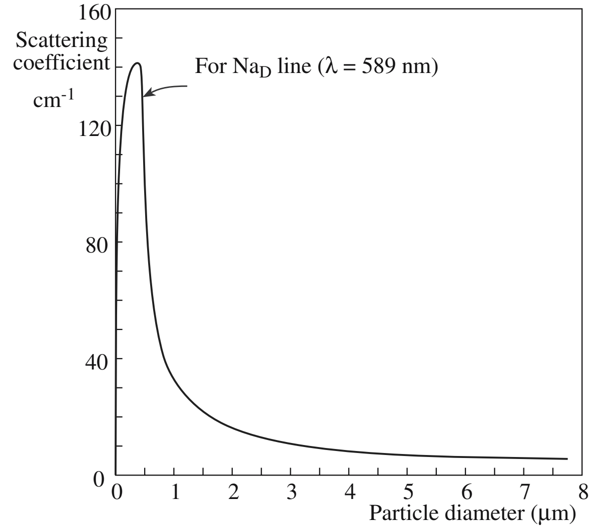

FIGURE 32.12 Effect of particle size on the scattering of light.

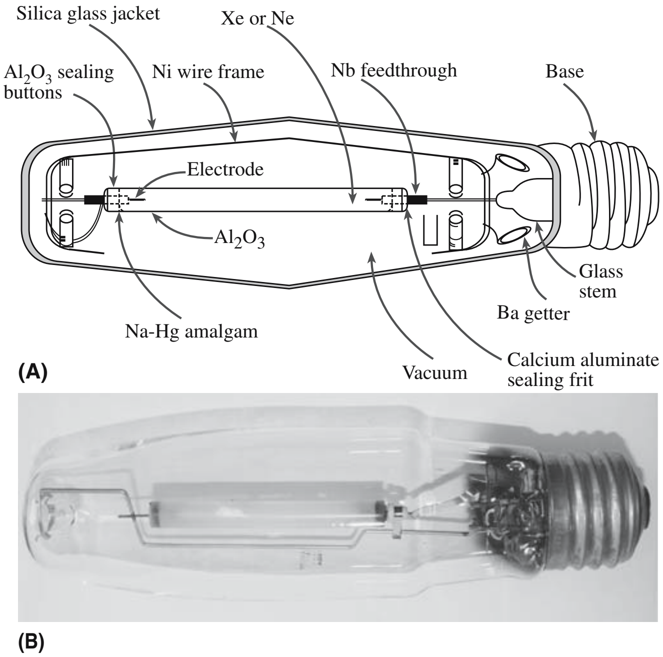

FIGURE 32.13 (a) Construction of an Na-vapor lamp. (b) An actual lamp.

TABLE 32.8 Fundamental Properties of Candidate Lamp-Envelope Materials

Property	*Al_2O_3*	*Y_2O_3*	*MgO*	*$3Al_2O_3 \cdot 2SiO_2$*	*$MgAl_2O_4$*	*$Y_3Al_5O_{12}$*
E_G (eV)	7.4	5.6	>5	≥5	>5	>5
σ (S/m)	$<2 \times 10^{-12}$	Low	Low	$<10^{-7}$	Low	Low
α (10^{-6} K^{-1}; 300–1300 K)	8.2	7.9	13.5	5.3	9.0	8.6
Strength (MPa)	310	150	206	270	184	410
$\mathcal{E}$ (GPa)	405	164	307	220	277	290
k at 300 K (W m^{-1} K^{-1})	29	13	25	6	15	13
R_{TS}	2707	1508	1242	1389	1077	2137
T_M (K)	2323	2737	3073	2101	2408	2243
Vapor pressure (Pa at 1500 K)	3×10^{-9}	1×10^{-10}	2×10^{-5}	2×10^{-5}	2×10^{-6}	—
Relative emissivity ($\sim\lambda_{0.75}$) (μm)	5.56	7.9	8.2	4	5.7	5.8

ceramic envelopes that did not contain any light-scattering porosity. The addition of small amounts of magnesia (MgO) allows us to sinter a compact of fine Al_2O_3 powder to theoretical density—free of porosity.

Table 32.8 compares the properties of Al_2O_3 to some of the other materials evaluated as candidate lamp-envelope materials. In addition to satisfying the materials selection criteria given above, Al_2O_3 also has a significant advantage over the other materials listed in Table 32.8 because it has superior thermal shock resistance.

32.10 FLUORESCENCE

Fluorescence occurs when light that is incident on a specimen causes the emission of light of another color; the effect is shown in Figure 32.14. This is most dramatic when the incident light is UV (and the observer is in a darkened room), but it also occurs with other wavelengths. Short wavelength UV is 254 nm; long wavelength UV is 300–388 nm (IR would be >780 nm). The wavelength of the emitted radiation is longer than that of the illuminating light; this is known as Stokes' law of fluorescence. The energy of the emitted light is therefore lower, with the difference in energy causing heating in the sample. Many naturally occurring minerals show fluorescence, but only some are spectacular.

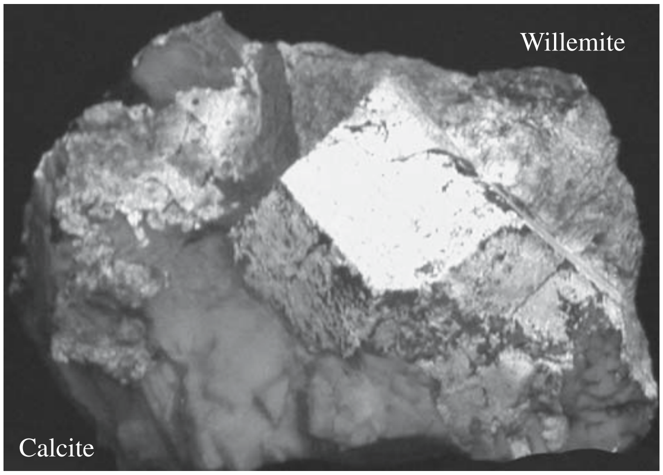

FIGURE 32.14 Fluorescent minerals.

Calcite, halite (with Mn)	red
Fluorite, opal	green
Adamite	yellow/green
Willhemite	green
Scheelite	blue
Scapolite	yellow

Scapolite has a complicated crystal structure and is formed by the alteration of plagioclase feldspars. Incidentally, diamond, sapphire, and ruby all fluoresce, but as with the materials above, the color depends on the UV wavelength used. A given specimen can also show different colors depending on the distribution of impurities. Trace elements can be included in synthetic gemstones to make them fluoresce and thus be easily identifiable.

Phosphorescence. UV radiation excites electrons to a higher energy state. When the UV is removed, the decay to the ground state usually takes seconds but can take years. A material that phosphoresces for 12 hours would have many uses (see Section 32.12).

Flash is the initial color produced when a UV lamp is first directed at certain fluorescent samples. The emitted wavelength then changes as exposure continues.

Thermoluminescence. This is essential fluorescence caused by heating a mineral to allow electrons that are trapped in high-energy states to drop back to the ground state. Heating chlorophane, a variety of fluorite, can produce a green light but only once.

Triboluminescence. Light can be produced by rubbing or striking a ceramic. Fracturing mica or rubbing a sphalerite crystal causes light emission.

Cathodoluminescence. Instead of UV radiation, this luminescence is produced by irradiating the sample with electrons (and therefore it usually occurs in a vacuum). This is the phenomenon used in cathode ray tubes (CRTs) (including old TV screens) that were coated on the inside with a ceramic phosphor.

32.11 THE BASICS OF OPTICAL FIBERS

Light is transmitted from one end of an optical fiber to the other by total internal reflection (TIR) as illustrated in Figure 32.15. Modern optical fibers use a composite construction with a core of refractive index n_1 and a cladding with a lower refractive index, n_2, such that $(n_1 - n_2)$ is typically in the range of 0.005–0.05. Light will remain in the fiber when the critical angle of incidence, i_c, is met or exceeded. To determine i_c we make use of Snell's law (which can be derived from Maxwell's equations):

$$n_2/n_1 = \sin i/\sin r \tag{32.8}$$

At i_c the angle of refraction, r, must be 90° and so we can write

$$n_2/n_1 = \sin i_c/\sin 90^\circ = \sin i_c/1 \tag{32.9}$$

The requirement for TIR sets a limit on the angle of the light incident on the fiber that will be trapped in the core of the fiber. This condition is expressed in terms of the numerical aperture (NA) of the fiber, defined as the sine of the acceptance angle for incident radiation.

$$\sin i_c = (n_2^2 - n_1^2)^{1/2} \tag{32.10}$$

Although light can be transmitted along a glass fiber in air, there are large losses due to scattering arising from surface defects on the fiber. The most important optical fibers consist of a high-purity glass core encased in an equally high-purity cladding. In most cases the cladding is glass, but polymer claddings are also used when a suitable glass cladding is not available or when it is important to reduce costs.

Kao and Hockham suggested the concept of sending optical signals along glass fibers in 1966. Initiated at the Standard Telecommunications Laboratory (STL) in the UK, optical fibers were crossing the Atlantic Ocean by 1988 and the Pacific Ocean by 1996 (but STL had disappeared). The first low-loss fibers were made at the Corning Glass Works. The fibers were made by a CVD process known as outside vapor-phase oxidation (OVPO) and produced an early fiber with a loss of 20 dB/km (which means that 1% of the light remains after traveling 1 km).

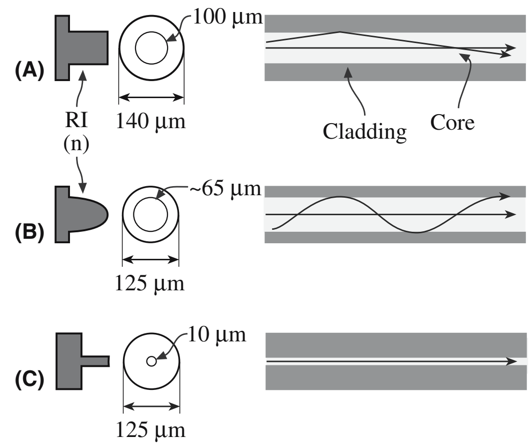

FIGURE 32.15 Total internal reflection (TIR) along an optical fiber. (a) Step index fiber; (b) graded index fiber; (c) single mode fiber. The plot on the left is a variation of RI (= *n*).

Materials

- Processing: how to make the fibers
- Applications: how they work and what goes wrong
- Materials: which glasses to choose

There are four classes of glass optical fiber.

1. Pure fused silica and doped silica glasses are used for telecommunications because of the requirement of very low transmission loss over long distances. These now form the backbone for trunk transmission in most developed countries, and in undersea intercontinental routes, and many millions of kilometers have been installed throughout the world. For applications in laser surgery pure silica-based glass fibers are used as they have a low transmission loss at 1.06 μm and have high strength and durability.

2. Multicomponent oxide glasses such as $Na_2O–CaO–SiO_2$ (NCS) and $Na_2O–B_2O_3–SiO_2$ (NBS) are used for applications requiring light transmission over short distances such as in image bundles, in optical faceplates on CRTs, and in IR imaging devices. The glass is of lower optical quality than silica glass, but can be processed in bulk by conventional melting techniques and is relatively cheap.

3. Fluoride glasses based on $ZrF_4–BaF_2–LaF_3–AlF_3–NaF$ (ZBLAN) have been widely investigated because they have potentially very low losses. The ultimate attenuation has been calculated to be $\sim 10^{-2}$ dB/km at 2.5 μm. Heavy-metal fluoride glasses are made by melting together high-purity fluoride powders at ~800°C and casting preforms. The impurity levels (~10–1000 ppb) have meant that the very low losses have not yet been achieved.

4. Chalcogenide glasses based on AsGeS have been investigated. The raw materials used to make these glasses are volatile and so the glasses are usually made in sealed silica ampoules in a rocking furnace. The resulting glass is reasonably stable and can be machined into preforms or drawn in a fiber from the melt.

Fabrication

Three methods are used to make glass optical fibers:

- Double crucible method
- Rod-in-tube method followed by drawing
- Chemical vapor deposition (CVD) techniques to make preforms followed by drawing

The double crucible method and the rod-in-tube method are used primarily for higher-loss fibers made from multicomponent glasses, such as those used in imaging bundles. Pure fused silica and doped silica fibers are drawn from a preform that has been made using a CVD process.

The *double-crucible method*: The glasses for the core and cladding are made by melting together the constituent oxides (or fluorides) and then pulling the fiber. This technique is suitable for glasses that have low working temperatures (<1200°C) such as NBS and NCS glasses.

The *rod-in-tube method*: A preform consisting of a rod of the core glass is formed inside a tube of the cladding glass. The preform can be made either by drawing a rod of core glass and a tube of cladding glass from the melt, or by machining a rod and tube from bulk glass. The preform is then drawn into a fiber by elongation in a furnace. Glass is drawn into a fiber when the viscosity is in the range of $10^3 - 10^5$ d Pa s. The drawing process, which is normally performed vertically downward, is a balance between the downward viscous forces and the surface tension of the molten region.

Several variations of the CVD process are used to make preforms:

- MCVD—modified chemical-vapor deposition
- OVD—outside vapor deposition
- VAD—axial vapor deposition

The MCVD process was developed by Bell Laboratories in the United States and became the standard method. The other processes are very similar except for the details of the geometry. The MCVD process is illustrated in Figure 32.16. The cladding is a tube of pure silica that is mounted in a special lathe. The core, which must have a higher *n* than the cladding, is formed inside the tube by the following reactions:

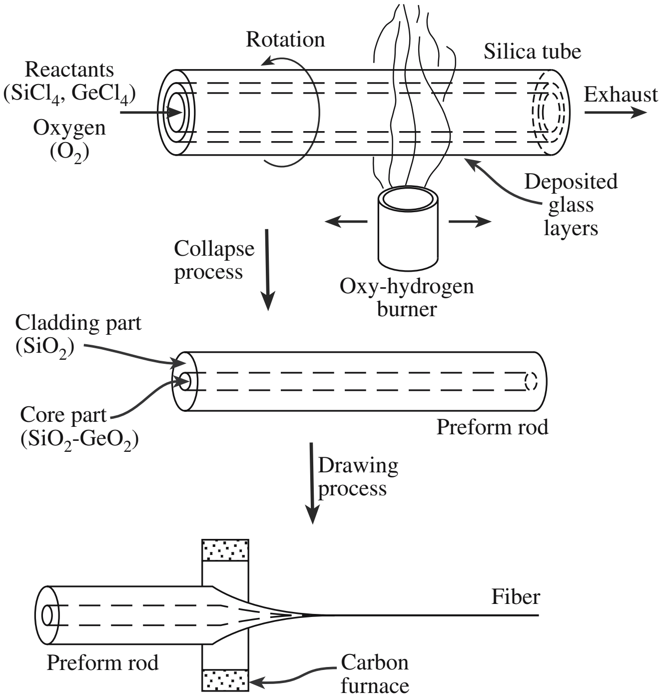

FIGURE 32.16 Steps in the metalorganic chemical vapor deposition (MOCVD) process for forming optical fiber preforms.

$$SiCl_4 + O_2 \rightarrow SiO_2 + 2Cl_2 \qquad (32.11)$$

and

$$GeCl_4 + O_2 \rightarrow GeO_2 + 2Cl_2 \qquad (32.12)$$

The burners that traverse the tube heat the vapors and oxidize the halides. Glass particles are deposited on the wall of the tube and are remelted to give clear glassy layers. The deposition rate is typically 1 g/min. When sufficient deposit has been achieved the tube is collapsed to give a preform. The GeO_2 has the effect of lowering *n*. Adding 10 mol% GeO_2 to pure SiO_2 raises *n* by 0.012. By varying the ratio of $GeCl_4$ to $SiCl_4$ in the gas stream with time it is therefore possible to produce graded-index fibers.

Drawing the Preform

The preform is drawn in a carbon-resistance furnace or zirconia induction furnace; these furnaces can provide the required temperature (>2000°C) while still having a reasonable operating life. The temperature required for drawing optical fibers is much greater than for conventional glass fibers because of their higher purity (the cladding is pure SiO_2). The furnace is mounted in a tall tower with a preform feed-screw mounted above. Drawing is achieved using a capstan, with the fiber being wound onto a drum that can hold several kilometers of fiber. A coating applicator is mounted above the capstan and fibers are coated on-line with a polymer to give mechanical protection. Drawing speeds of >10 m/s are possible in production; the drawing speed is mainly limited by the stability of the polymer coating process. A single preform can yield up to 100 km of fiber. A schematic of a typical fiber drawing apparatus is shown in Figure 32.17.

Silica fibers may be joined in an electric arc. The two ends are aligned and the arc is struck. The fibers are fed toward each other at a controlled rate so they are fused with minimal distortion of the core; joint losses can be very low (<0.1 dB). We then have to polish the ends of the fiber.

Operation

An important characteristic for optical fibers is loss or attenuation. Attenuation in fibers is normally measured in decibels per kilometer (dB/km). The optical loss, in dB, measured over 1 km is written as 10 log I_{in}/I_{out} where I_{in} and I_{out} are the input and output optical power.

The optical signal can be attenuated primarily by two factors.

1. *Absorption*. Photons interact with electronic and vibrational transitions in the glass in the UV and IR regions, respectively. In the UV, absorption is due to electronic transitions across the band gap. Absorption occurs at shorter wavelengths for a larger band gap. In the IR, absorption is due to a coupling of the electromagnetic field to lattice vibrations.

2. *Scattering*. Fluctuations in composition and density of the glass occur as it cools down below T_g; the resulting scattering is a form of Rayleigh scattering. We can describe the intrinsic loss, L, mathematically by

$$L = A\ \exp(e/\lambda) + B\ \exp(-g/\lambda) + C\lambda^{-4} \quad (32.13)$$

where A, B, C, e, and g are constants characteristic of the glass. These loss mechanisms combine to give a loss spectrum as shown in Figure 32.18. For silica the minimum loss of 0.15 dB/km occurs at a wavelength of 1.55 μm. ZBLAN is a fluoride glass with even lower loss, 0.02 dB/km at 2.55 μm. These losses are theoretical minima and difficult to achieve in practical situations.

There are many extrinsic sources of loss:

- Absorption caused by transition metal impurities (e.g., Fe, and Cu)

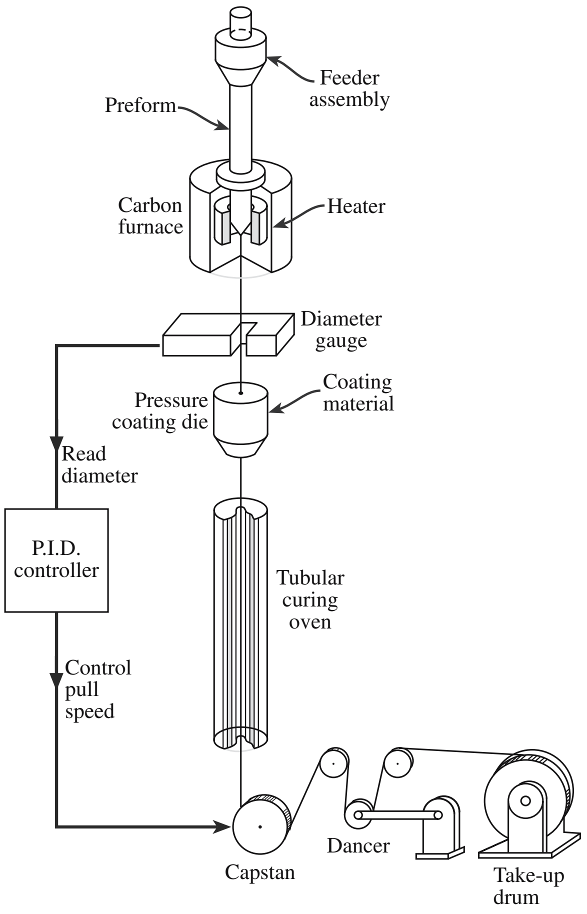

FIGURE 32.17 The fiber drawing tower.

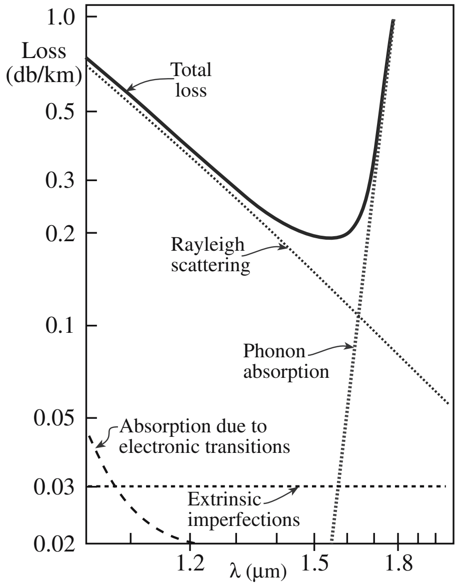

FIGURE 32.18 Loss spectrum for fibers.

- Absorption caused by the OH group
- Scattering caused by defects in the glass such as particulate contamination and bubbles
- Scattering caused by manufacturing defects such as changes in the fiber diameter along its length and frozen-in stresses

The minimum loss in commercial silica fibers used for optical communications is typically 0.2 dB/km at 1.55 μm. In fluoride fibers the lowest reported loss is 0.4 dB/km at 2.35 μm.

32.12 PHOSPHORS AND EMITTERS

When a material is placed in an electric field or irradiated with light, it may itself radiate light: either electric or optical energy is absorbed and optical energy is then radiated. A material that exhibits this phenomenon is called a phosphor and the light radiated is called luminescence (see Section 32.10). Luminescence can be fluorescence or phosphorescence. The difference is the time for which emission occurs.

- Fluorescence occurs very quickly: $<10^{-8}$ s.
- Phosphorescence is slow emission over ~1 s or even longer.

Table 32.9 lists the applications of various phosphors.

Light-emitting diodes and III–V lasers are devices that use a direct-band-gap semiconductor to convert electrical energy into visible light. They have long been used for materials with $E_g \sim 1$ eV (the familiar red), but now GaN (with a wider band gap, large ν, and smaller λ) gives us a blue emitter.

TABLE 32.9 Applications of Various Phosphors

Applications	*Excitation methods*	*Phosphors*	*Color*
Color TV	18–27 kV e-beam	ZnS: Ag, Cl	Blue
		ZnS: Cu, Au, Al	Green
		Y_2O_2S: Eu	Red
Cathode ray tube	1.5–10 kV e-beam	Zn_2SiO_4: Mn	Green
Electron microscope	50–3000 kV e-beam	(Zn,Cd)S: Cu, Al	Green
Numerical display	~20 kV e-beam	ZnO	Green
Fluorescent lamps	254 nm UV	$Ca_{10}(PO_4)_6(F,Cl)_2$: Sb, Mn	White
Fluorescent Hg lamps	365 nm UV	$Y(V,P)O_4$: Eu	Red
Copying lamps	254 nm UV	Zn_2SiO_4: Mn	Green
X-ray multipliers	X-ray	$CaWO_4$	Blue/white
		Gd_2O_2S: Tb	Yellow/green
Scintillators	Radiation	NaI: Tl	Blue
Electroluminescence	10–5 × 10 ac/dc	ZnS: Cu, Mn, Cl	Green
Solid-state lasers	Visible light (near UV – near IR)	$Y_3Al_5O_{12}$:Nd (YAG)	IR

32.13 SOLID-STATE LASERS

The word “laser” was originally an acronym for “light amplification by the stimulated emission of radiation”; now it is just a word—so there is no capitalization. A laser produces coherent (in phase) monochromatic (single λ) radiation. It consists of the active medium, called the optical cavity, which in the case of a solid-state laser is an insulating crystal or glass containing a specific dopant. The optical cavity is typically 10 cm long and 1 cm in diameter. One end is coated to form a partially transparent mirror while the other end is fully reflecting. The operation of the laser is based on electronic excitation of the active medium using a pump source, which is usually a flash lamp or flash tube, as shown in Figure 32.19, or another laser. The excited electrons relax back to the ground state by emitting light. As light is reflected to and fro between the mirrors it is amplified.

The two most important solid-state lasers are:

1. The ruby laser uses a single crystal of Al_2O_3 containing about 1.6×10^{19} Cr^{3+}/cm^3. The active electronic states are d levels of the Cr^{3+}.

NOTATION

$^4I_{11/2}$ is an example of a term symbol having the form $^{2S+1}L_J$, which is used to describe arrangements of electrons in orbitals. The superscript is $2S + 1$ where S is the overall spin $S = \Sigma m_s$. The symbol is the overall $L = \Sigma m_l$. The subscript is a quantum number, J, that considers spin-orbit coupling; J has values from $L + S$, $L + S - 1$, to $|L - S|$.

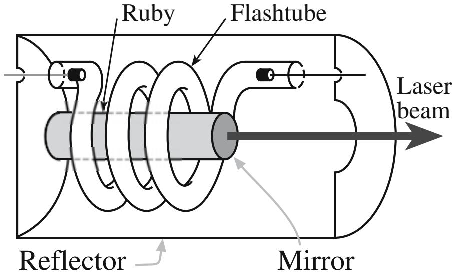

FIGURE 32.19 Schematic of the components of a ruby laser.

2. The Nd–YAG laser uses a single crystal of $Y_3Al_5O_{12}$ containing 1.4×10^{20} Nd^{3+}/cm^3. The active electronic states are the f levels of Nd^{3+}.

The properties of the ruby and Nd–YAG laser are summarized in Table 32.10. The Cr^{3+} transition is a three-level system: the laser transition returns the electrons to the ground state. The emission occurs in the red part of the visible spectrum (λ = 694 nm). The Nd^{3+} transition is a four-level system: emission occurs near 1.06 µm and the terminating state lies above the

TABLE 32.10 Characteristics of Typical Solid-State Laser Crystals

Crystal	*Active center*	*Concentration of active centers (cm^{-3})*	*Spontaneous fluorescence lifetime*	*Wavelength*
Ruby	Cr^{3+}	1.6×10^{19}	3 ms	694.3 nm
YAG : Nd	Nd^{3+}	1.4×10^{20}	230 µs	1.061 µm, 1.064 µm, 1.839 µm (77 K), 0946 µm (77 K), 1.318 µm
NaF–(F_2^+)	(F_2^+) color center	2×10^{17}	40 ns	Tunable, 0.99–1.22 µm
$Nd_{0.5}La_{0.5}P_5O_4$	Nd^{3+}	2×10^{21}	150 µs	1.05 µm

ground state. The four-level system is shown schematically in Figure 32.20.

Doped oxide glasses are also used as the optical cavities in solid-state lasers. A wide range of dopants and glasses can be used as indicated in Table 32.11. The advantages of using glass as a laser medium is that glass is optically isotropic and producible in a variety of sizes and shapes of high optical quality. In addition, its chemical composition can be varied to tailor laser parameters for specific applications. However, because the thermal conductivity of glass is usually poor compared to its crystalline counterparts, glass lasers are limited to pulsed and low average-power operation. Crystalline lasers are more appropriate for continuous and high-average-power operation.

POLING

Poling is the process of polarizing a ferroelectric material by applying a high electric field for a short time.

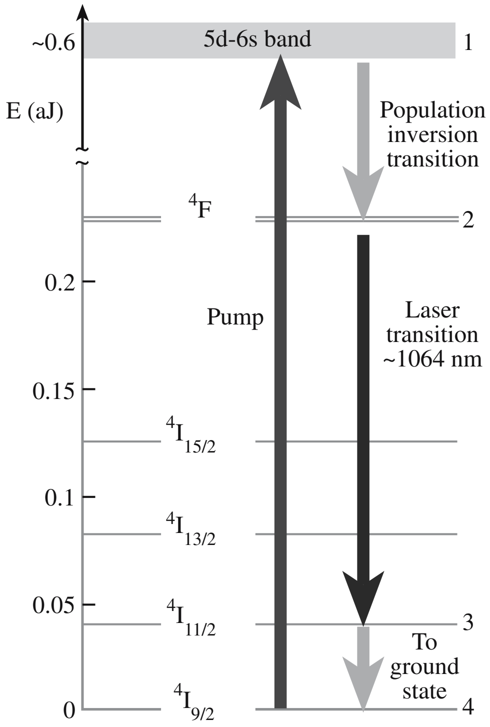

FIGURE 32.20 The four-level system for lasers.

32.14 ELECTROOPTIC CERAMICS FOR OPTICAL DEVICES

Electrooptic Effect

By applying an *E* field the optical properties, especially *n*, of electrooptic (EO) materials can be changed. Many transparent solids and liquids show EO effects, but only a few of these are useful for practical applications.

If an electrooptic ceramic is noncentrosymmetric then δn is proportional to E. Examples of such materials include piezoelectric crystals and some poled ferroelectric ceramics; this is known as the linear or Pockels effect. If the material is initially centrosymmetric, then δn is proportional to E^2; this is known as the quadratic or Kerr effect. Such materials include isotropic crystals, unpoled ferroelectric ceramics, and all liquids.

We saw in Section 32.1 that EO materials are birefringent: i.e., they have two orthogonal optic axes that are characterized by different indices of refraction; Δn is referred to as the birefringence in Eq. 32.5. The value of Δn may be positive or negative. If an *E* field is applied parallel to one optic axis, then one refractive index is changed with respect to the other. As a result Δn is changed and the state of polarization of light propagating through the material is altered. Quadratic EO materials are not generally birefringent unless they are subjected to a properly aligned *E* field.

The general relationship between Δn and *E* is

$$\Delta n = n^3(r_c E + RE^2) \tag{32.14}$$

Table 32.12 lists the values of *r* and *R* for several EO ceramics. The higher the EO coefficient, the lower the applied voltage necessary to perform a particular function.

TABLE 32.11 Glass Laser Ions and Hosts

Ion	*Transition*	*Wavelength (μm)*	*Sensitizer*	*Host glasses*
Nd^{3+}	$^4F_{3/2} \rightarrow {}^4I_{9/2}$	0.92		Borate, silicate (77 K)
	$^4F_{3/2} \rightarrow {}^4I_{11/2}$	1.05–1.08	Mn^{2+}, UO_2^{2+}	Borate, silicate, phosphate, fluorophosphates, germanate, tellurite, fluoroberyllate
	$^4F_{3/2} \rightarrow {}^4I_{13/2}$	1.32–1.37		Borate, silicate, phosphate
Tb^{3+}	$^5D_4 \rightarrow {}^7F_4$	0.54		Borate
Ho^{3+}	$^5I_7 \rightarrow {}^5I_8$	2.06–2.08	Yb^{3+}, Er^{3+}	Silicate
Er^{3+}	$^4I_{13/2} \rightarrow {}^4I_{15/2}$	1.54–1.55	Yb^{3+}	Silicate, phosphate, fluorophosphate
Tm^{3+}	$^3H_4 \rightarrow {}^3H_6$	1.85–2.02	Yb^{3+}, Er^{3+}	Silicate
Yb^{3+}	$^2F_{5/2} \rightarrow {}^2F_{7/2}$	1.01–1.06	Nd^{3+}	Borate, silicate

TABLE 32.12 Electrooptical Properties of Several Ceramics

Material	κ	n *at 633 nm*	r_c *m/V*	R *m²/V²*
Ceramic				
PLZT 8.5/65/35	5000	2.50	—	38.6×10^{-16}
PLZT 9/65/35	5700	2.50	—	3.8×10^{-16}
PLZT 9.5/65/35	5500	2.50	—	1.5×10^{-16}
PLZT 8/70/30	5400	2.48	—	11.7×10^{-16}
PLZT 8/40/60	980	2.57	1.02×10^{-10}	—
PLZT 12/40/60	1300	2.57	1.20×10^{-10}	—
PLZT 14/30/70	1025	2.59	1.12×10^{-10}	—
Single crystal				
$LiNbO_3$ (r_{33})	37	2.20	0.32×10^{-10}	—
$LiNbO_3$ (r_{13})	37	2.29	0.10×10^{-10}	—
$BaTiO_3$ (r_{33})	373	2.36	0.28×10^{-10}	—
$BaTiO_3$ (r_{51})	372	2.38	8.20×10^{-10}	—
$KNbO_3$ (r_{33})	30	2.17	0.64×10^{-10}	—
$KNbO_3$ (r_{42})	137	2.25	3.80×10^{-10}	—
Strontium barium niobate ($T = 560\,K$)	119	2.22	0.56×10^{-10}	—
Strontium barium niobate ($T = 300\,K$)	3400	2.30	13.40×10^{-10}	—
$Ba_2NaNb_5O_{15}$	86	2.22	0.56×10^{-10}	—

Solid Solutions in the PLZT System

The most important EO ceramics are solid-solution phases in the $PbZrO_3$–$PbTiO_3$–La_2O_3 system known collectively as PLZT materials.

- The general chemical formula is $Pb_{1-x}La_x(Zr_zTi_{1-z})_{1-x/4}O_3$.
- The structure of PLZT is based on the perovskite, ABO_3 (see Section 7.3).

The linked network of oxygen octahedra has B ions (Ti^{4+}, Zr^{4+}) occupying the sites within the oxygen octahedra (B sites) and A ions (Pb^{2+}, La^{3+}) situated in the interstices (A sites) created by the linked octahedra. When off-valent ionic substitutions are made into this structure (e.g., La^{3+} for Pb^{2+}) electrical neutrality is automatically maintained by the creation of A-site or B-site vacancies.

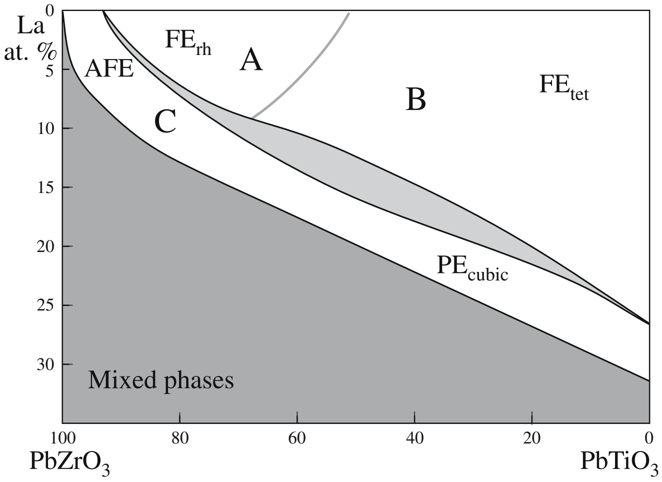

FIGURE 32.21 The PLZT phase diagram. A, memory; B, linear; C, quadratic.

The PLZT phase diagram at room temperature is shown in Figure 32.21. The compositions are specified by three successive numbers, e.g., 8.5/65/35, which represent, from left to right, the La, Zr, and Ti atomic concentrations.

PLZT COMPOSITION

When expressed as 8.5/65/35, the PLZT contains 8.5 at% La and the Zr/Ti ratio is 65/35.

Ferroelectric PLZT ceramics possess crystalline phases that belong principally to the tetragonal and rhombohedral crystal systems. These materials are classified as uniaxial, because they have two or more crystallographically equivalent directions lying in a plane that is perpendicular to the 4-fold (tetragonal case) or 6-fold (rhombohedral case) axis. They are also optically negative (i.e., $n_e – n_o < 0$), with Δn values typically ranging from about −0.018 to near zero. These values are low because of the low distortion of the unit cell. In their ferroelectric (FE) state the polar *c* axis is typically only about 1% longer than the *a* axis, which is why domain reorientation is easy in these materials. Domain reorientation produces a change in the optical properties. The magnitude of the observed EO effect is dependent on both the strength and direction of the *E* field.

PLZT ceramics display optically uniaxial properties on both a microscopic and a macroscopic scale once polarized. The optic axis coincides with the polarization.

TABLE 32.13 Transparent Electrooptical Ceramics

Composition	*Notation*	*Composition*	*Notation*
$(Pb,La)(Zr,Ti)O_3$	PLZT	$(Pb,La)(Hf,Ti)O_3$	PLHT
$(Pb,Ba,Sr)(Zr,Ti)O_3$	PBSZT	$(Pb,Sn)(In,Zr,Ti)O_3$	PSIZT
$(Pb,Ba,La)Nb_2O_6$	PBLN	$(Pb,La)(Zn,Nb,Zr,Ti)O_3$	PBLNZT
$K(Ta,Nb)O_3$	KTN	$Pb(Sc,Nb)O_3$	PSN
$(Pb,La)(Mg,Nb,Zr,Ti)O_3$	PLMNZT	$(Ba,La)(Ti,Nb)O_3$	BLTN
$(Pb,La,Li)(Zr,Ti)O_3$	PLLZT	$(Sr,Ba)Nb_2O_6$	SBN

The macroscopic or effective birefringence is designated by $\overline{\Delta n}$. On a macroscopic scale, $\overline{\Delta n}$ is equal to zero before electrical poling and has some finite value after poling, depending on the composition and the degree of polarization. The $\overline{\Delta n}$ value is an important quantity because it is related to the *optical phase retardation*, Γ, of the material.

The phenomenon of optical phase retardation in an EO poled ceramic occurs when entering linearly polarized monochromatic light is resolved into two perpendicular components c_1 and c_2. Because of the different refractive indices, n_e and n_o, the propagation velocity of the two components will be different and will result in a phase shift or "retardation." Γ is a function of both $\overline{\Delta n}$ and the path length t:

$$\Gamma = \overline{\Delta n}t \tag{32.15}$$

Although at present PLZT is the most important EO ceramic, there are other transparent ceramics that exhibit EO characteristics; some of these are listed in Table 32.13. Many of these ceramics are based on solid solutions in the lead zirconate–lead titanate (PZT) system and are structurally related to PLZT. Notable exceptions are the niobates, such as KTN (potassium tantalum niobate or $KTa_{1-x}Nb_xO_3$ with $x \sim 0.35$), which are also based on the perovskite structure. NTT has shown n for KTN changing by a factor of 20× the change produced in $LiNbO_3$ using an applied field of 60 V/mm^2 (achieved by applying 1.2 V across a 20-μm sample), but the limiting factor is the growth of high-quality crystals.

Electrooptic Characteristics of PLZT Ceramics

Depending on composition PLZT ceramics display one of the three major types of EO characteristics shown in Figure 32.22.

1. *Memory.* The P versus E hysteresis loop is narrow, indicating low E_c. This characteristic occurs for the rhombohedral FE phase; a typical composition is 8/65/35. The EO memory effect depends on the fact that $\overline{\Delta n}$ can be set to different values by applying (and removing) an E field. Once set, $\overline{\Delta n}$ remains constant as long as $E = 0$. The variation of $\overline{\Delta n}$ is usually plotted in terms of the normalized remnant polarization P_r/P_R because P_r is an easily measured parameter that depends on domain switching. Intermediate remnant states can be achieved by removing the applied E field prior to reaching E_c.

2. *Linear* (Pockels effect). This effect is characterized by a square hysteresis loop having a large E_c. It occurs for tetragonal type compositions at the $PbTiO_3$-rich end of the solid-solution range such as 8/36/60. $\overline{\Delta n}$ is linear with respect to E; from a practical point of view, grain size has a very significant effect on the linearity.

3. *Quadratic* (Kerr effect). A slim hysteresis loop with zero, or very low P_r, is obtained between the FE and paraelectric (PE) compositions; a typical composition is 9.5/65/35. At room temperature they are essentially cubic, but the application of E enforces a transition to the rhombohedral or tetragonal FE phase, and the optical anisotropy increases with E^2.

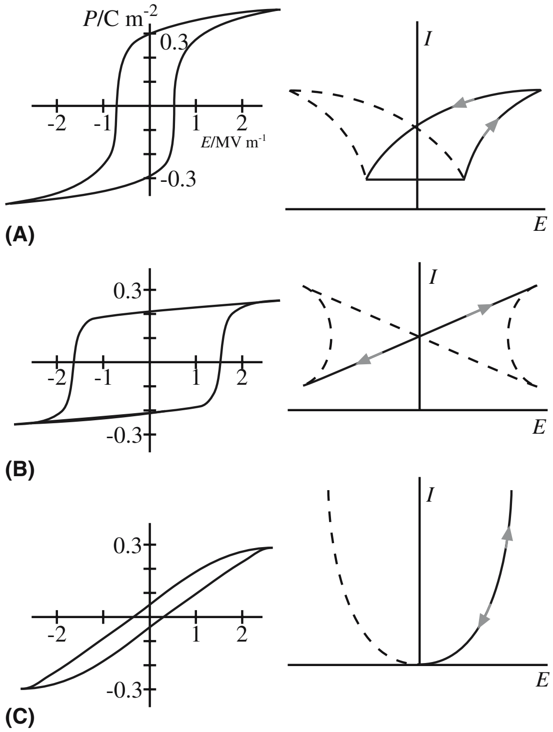

FIGURE 32.22 Electrooptic characteristics of PLZT: (a) memory, (b) linear, (c) quadratic. *I* is the light output versus applied field *E* (see A, B, and C in Figure 32.21).

Making Transparent PLZT Ceramics

For a ceramic to be useful as an EO material it must be transparent. In single-crystal form ferroelectric materials possess high optical transparency and useful EO properties. In the form of polycrystalline ceramics they can also possess such properties if special precautions are taken during processing. To create a transparent ceramic it is necessary to limit the amount of sources that can lead to light scattering (the main culprits were discussed in Section 32.8). Hot pressing can produce a high-density product with low porosity. If the pore size is reduced to a value less than the wavelength of light ($\lambda_{\text{yellow}} \sim 0.5\,\mu\text{m}$) then the pores will have only a minor scattering effect. The presence of impurities can be reduced by using high purity starting materials or by preparing the powders by a sol-gel process using metal alkoxides (see Chapter 22). The use of liquid or solution techniques also helps to ensure good intermixing between the various components. As noted above, for noncubic materials light scattering can occur at GBs, where refractive indices are discontinuous. In PLZT the optical anisotropy is reduced by doping with La, which brings the ratio between *c* and *a* lattice parameters close to unity.

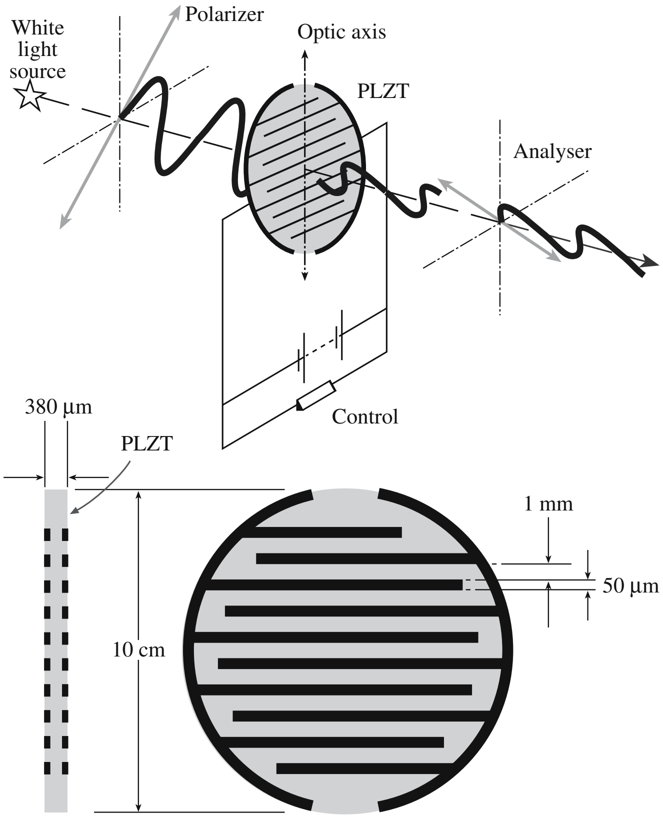

FIGURE 32.23 Illustration of the operation of flash goggles and the interdigitated electrode arrangement.

Applications Using PLZT Electrooptic Ceramics

There are several applications for EO ceramics and two basic modes of operation for EO devices.

- Transverse—the *E* field is applied in a direction normal to the light propagation direction.
- Longitudinal—the *E* field is applied along the light propagation direction.

Linear materials are used primarily for high-speed modulation of the intensity, amplitude, phase, frequency, or direction of a light beam. Quadratic materials are used principally for light valves and shutters.

Here we will briefly describe four applications for PLZT ceramics.

1. Flash goggles are used by military pilots to prevent them from being blinded by a very bright flash! The arrangement consists of three components as illustrated in Figure 32.23. Under normal illumination the PLZT plate allows the plane of polarization to be turned by 90° when a voltage of ~800 V is applied to the interdigitated gold electrodes. The light passes through the analyzer and into the pilot's eyes. An intense flash of light is detected by a photodiode that forms part of the circuit connected to the PLZT plate, and removes the voltage applied to the electrodes. The plane of polarization of the incident light is not rotated and the analyzer blocks most of the light. The switching times are ~100 µs and transmission ratios are 1000 : 1. For this application the PLZT is a slim-loop quadratic material of typical composition 9.2/65/35, with almost zero birefringence when $E = 0$.

This application uses an arrangement similar to that used for a voltage-controlled color filter. Now a variable voltage is used that determines what part of the visible spectrum is blocked. When the applied voltage is zero no light is transmitted. At the voltage at which the green light is retarded by $\lambda/2$ "white" light is transmitted (i.e., green plus part of everything else). Further increases in the voltage produce conditions at which the blue is extinguished resulting in the transmission of yellow light (i.e., red and green are transmitted). In a similar way voltage conditions can be reached at which either the red or the green is excluded and the resulting colors are transmitted. Again the PLZT is of the slim-loop quadratic variety.

2. PLZT elements can be used in reflective displays as shown in Figure 32.24. P_1 and P_2 are polarizers that are set up in the parallel position. When no voltage is applied to the indium tin oxide (ITO) electrodes, light passes through both polarizers and the PLZT plate and is reflected from the reflecting surface into the eye. If a voltage (~200 V) is applied to the PLZT the light experiences a retardation of $\lambda/2$ and is extinguished at P_2. The activated segments appear dark against a light background. The PLZT is again of the 9.5/65/35 type, so it has a slim-loop quadratic. PLZT displays are much more expensive and

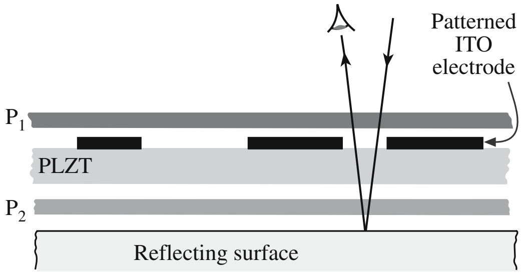

FIGURE 32.24 Basic layout of a PLZT reflective display.

require much higher operating voltages (>100 V) than the liquid crystal variety, but offer faster switching times. The main applications are in military and automotive markets.

3. Figure 32.25 shows an image storage device using PLZT that operates on the basis of light scattering by domain boundaries in the unpoled material. The PLZT is of the memory type with a composition 7/65/35 and a grain size of ~4.5 μm. To start, the device is uniformly irradiated and the PLZT is poled to P_r. The image to be stored is focused onto the photoconductive film (e.g., CdS or ZnS) while a voltage (~200 V and opposite to that of the poling voltage) is applied across the transparent electrodes. This causes regions of the ferroelectric to become depoled. The image can then be read by passing light through the plate and focusing the unscattered light so that it passes through an aperture and onto a film. Regions that have become depoled scatter the light to a greater extent than the poled regions. Repoling the PLZT can erase the display.

4. Optical signals in telephone systems are routed by first converting them to their electronic equivalents, switching them electronically, and then reconverting them to the optical form. Thin-film optical switches allow the process of switching to be done optically, avoiding the need for electronic conversion. An example of a thin film optical switch using PLZT is shown in Figure 32.26. The PLZT layer can be deposited onto the sapphire substrate by a variety of methods including sputtering, CVD, and sol-gel. The lattice mismatch between the (0001) plane of sapphire and (111) plane of the PLZT is quite small (~2%), and this facilitates the formation of an epitactic layer with the planar relationship $(0001)_s \| (111)_{PLZT}$.

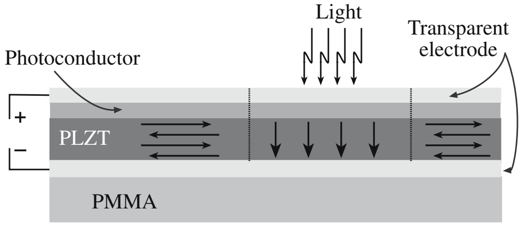

FIGURE 32.25 Schematic of an image storage device using a field-induced polarized PLZT film.

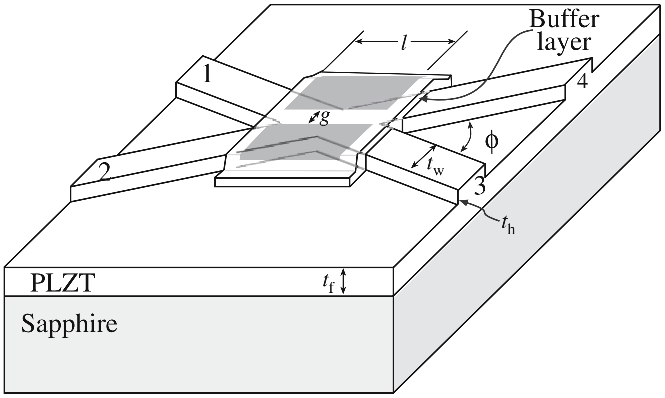

FIGURE 32.26 An example of a PLZT thin film optical switch on sapphire.

When there is no voltage applied to the metal electrodes light entering at 1 will exit at 3. If a large enough voltage V is applied, total internal reflection (TIR) of the light will occur between the electrodes causing the signal to now exit at 4. TIR occurs because the voltage reduces n.

The critical angle for TIR is

$$\theta_c = \sin^{-1}(1 - 0.5n^2RV^2) \tag{32.16}$$

The change in n causing TIR is regarded as being due to the Kerr effect. If we use a 9/65/35 quadratic PLZT with $R = 380\,\text{nm}^2/\text{V}^2$, $n = 2.5$, and with a 2° angle between the guides (i.e., $\theta_c = 88°$) then the switching voltage is 1.4 V.

32.15 REACTING TO OTHER PARTS OF THE SPECTRUM

So far we have concentrated on how ceramics interact with light in the UV, visible, and IR parts of the spectrum. This emphasis is because these interactions are often the most useful and the ones that we are likely to notice. The response of ceramics to γ-rays is becoming of increased interest because of their use for radiation detectors (primarily aimed at locating radioactive material that might be used for "dirty bombs"). Ceramics have long been used to detect high-energy radiation. One example is Tl-doped NaI used as a scintillation detector on early X-ray diffractometers. The thallium causes the crystal to fluoresce in the violet part of the spectrum (λ = 420 nm). The goal is to make lower cost devices that can be portable, for example, incorporated into pagers and cell phones.

The basic requirements of a scintillator for γ-rays are as follows:

- High light yield (>20 k photons generated per incident γ-ray)
- A fast response time (<100 ns)
- High density and high Z
- Scintillation λ matches that of the light sensor (usually an Si diode or photomultiplier)

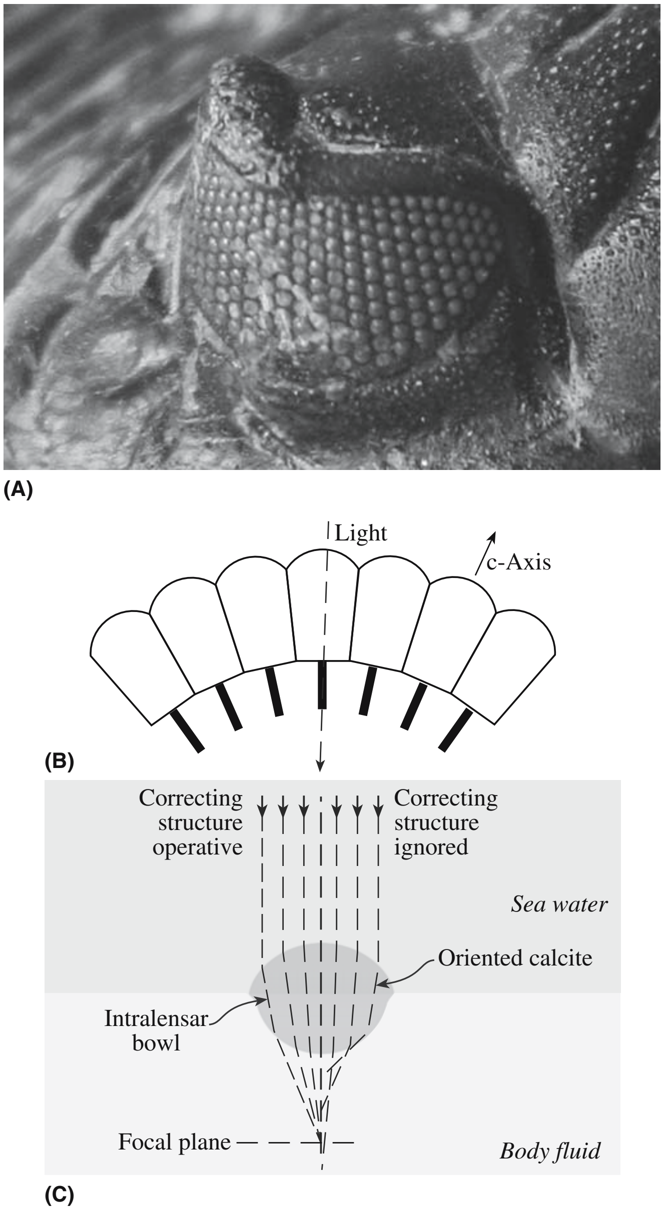

FIGURE 32.27 Trilobite eye.

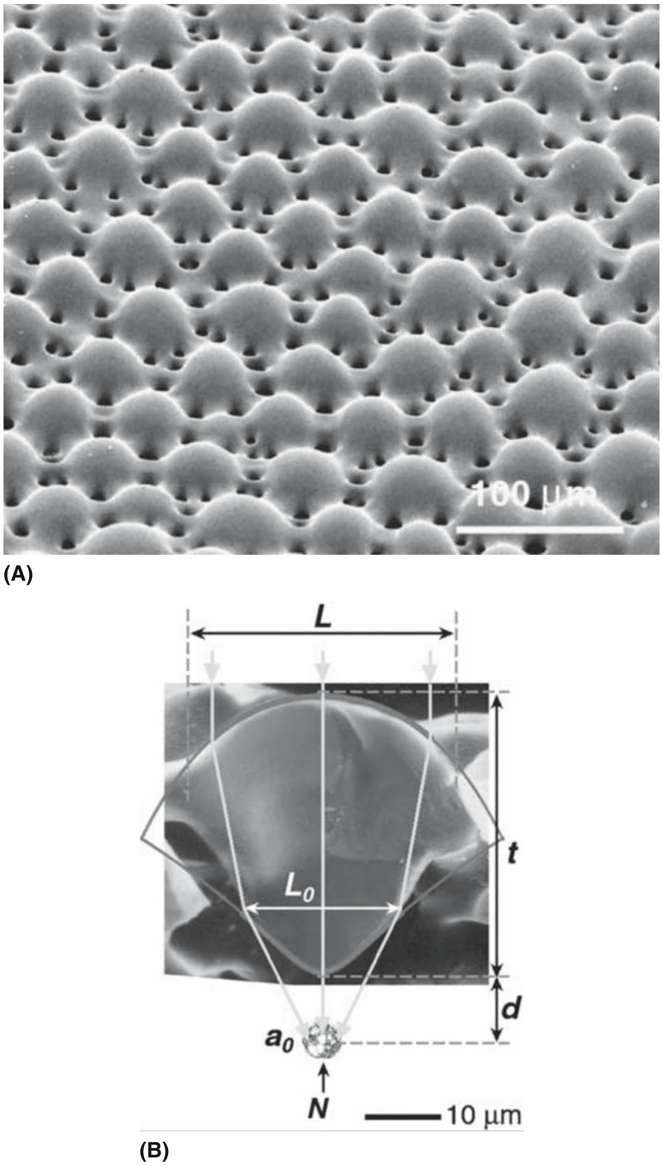

FIGURE 32.28 The brittlestar lens: (a) plan view of an array; (b) cross section.

Ce-doped YAG (which is yellow) is one ceramic that meets these requirements and the estimated cost for single crystals is <\$0.05 mm^{-3}.

32.16 OPTICAL CERAMICS IN NATURE

We will use many of the concepts introduced in this chapter when we discuss gemstones in Chapter 36. Nature does make use of these concepts in surprising ways. Figure 32.27 shows the eye of a trilobite. Trilobites existed for over 300 million years. The eye shown here is an array of calcite crystals, which direct the light to a point. So at least some of the trilobites could see because their eyes were inorganic crystals. We may think of this as being an oddity because the trilobites are extinct (although they did survive for ~300 million years). However, it has now been shown that brittlestars use a similar structure to detect light. The scanning electron microscopy (SEM) image in Figure 32.28 shows an array of calcite lenses on the surface of the dorsal arm plate. The cross section through one of these lenses demonstrates how the light is focused onto the nerve and even how the spherical aberration is corrected.

ECHINODERMATA

This is a group of animals that includes sea urchins and sea stars, one of which is the brittlestar (*Ophiocoma wendtii*).

CHAPTER SUMMARY

At the simplest level the optical properties of ceramics are critical to society because glass is transparent, diamonds are not opaque, the development of television required phosphors, nearly all lighting depends on glass, the future of communications relies on glass fibers and periodic amplifiers, etc. Microscopy developed using glass lenses and led to our understanding of biology. We tend to use color when glazing (or there are no patterns). The general idea is that light affects and is affected by the electrons in the ceramic and this interaction is determined by the bonding in the ceramic. The interaction actually causes the speed of light to change inside a ceramic. The key properties of the material are then described by average quantities such as the dielectric constant and the refractive index. Crystallography comes in again because many ceramics are anisotropic; one particularly well-known case is calcite.

PEOPLE IN HISTORY

Coble, R.L. (Bob) (1928–1992) developed Lucalox®, a transparent polycrystalline alumina (Al_2O_3) ceramic, at the GE laboratory in Schenectady in 1961; GE is still a major supplier of lamp envelopes but Silvania, Osram and others also manufacture the envelopes now.

Maxwell, James Clerk (1831–1879) developed the electromagnetic wave theory of light.

Seabright, Clarence A. (1914–2002) in the United States was one of the key contributors to the development of ceramic pigments: (1948) Ceramic Pigments, US Patent 2,441,367; (1961) Yellow Ceramic Pigments, US Patent 3,012,898; (1965) Iron Ceramic Pigment, US Patent 3,166,430.

van Royen, Willebrod Snell (1581–1626), the Dutch scientist, first described Snell's law; the derivation is given in standard textbooks on electromagnetism (Panofsky and Philips, 1961) or optics (Born and Wolf, 1970).

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WWW

Saphikon (www.saphikon.com) gives current examples of using alumina fibers in medicine.

EXERCISES

32.1 Explain why $BaTiO_3$ is a linear electrooptic material below T_c but a quadratic electrooptic material above T_c.

32.2 PLZT ceramics belonging to either the tetragonal or rhombohedral crystal systems are classified as optically uniaxial. Which other crystal system or systems are also optically uniaxial?

32.3 Several methods have been used to produce PLZT thin films. Try to find as many methods as you can and discuss the pros and cons of each.

32.4 Prior to the development of transparent alumina ceramics the material of choice for the lamp-envelope market was silica-based glass. Explain why such materials are not suitable for use in the sodium vapor lamp but dominate the incandescent, fluorescent, and electric discharge lamp-envelope market.

32.5 With the increasing demand for optical fiber communication systems new glass and fiber processing methods are being investigated. One such example is the sol-gel route for silica fibers. What advantages do you think the sol-gel route would offer over the present CVD processes? Can you think of any disadvantages of the sol-gel route?

32.6 The single crystals required for solid-state lasers are often made by the Czochralski process. Describe the advantages and disadvantages of using this process for producing single crystals of ruby and YAG.

32.7 Explain briefly why the transparency range of single crystal NaCl is much greater than for single crystal MgO.

32.8 Why are house bricks different colors? (You can answer this in 2 minutes or 2 hours.)

32.9 How is the numerical aperture (NA) of a fiber linked to the NA of a camera lens?

32.10 What causes refraction in glass?