

Optical Materials for Infrared Spectroscopy

D. Warren Vidrine

Vidrine Consulting, San Juan Capistrano, CA, USA

1 INTRODUCTION

Infrared (IR) spectroscopy is unique among the high-information-content spectroscopies in its ability to measure easily all states of matter. Even better, it can do this with the sample segregated from the inner workings of the instrument (unlike mass spectrometry and chromatography). Nonetheless, the sample must be sampled somehow, so the Achilles' heel of IR spectroscopy is the requirement for interfacial materials which transmit and/or reflect IR light over a broad spectral region.

In near-IR, visible, and ultraviolet (UV) spectroscopy we take the abundant virtues of plastics, glass, and fused quartz for granted, but in the mid-IR region no such "perfect" materials exist and it is difficult to achieve even two qualities out of the "good, cheap, easy" trilogy. This article is intended as a critique of the optical materials commonly utilized in IR-sample interface systems, along with some comments about their practical implementation.

Several reference books have extensive tables of properties for mid-IR optical materials, but there it is difficult to find the salient properties assembled in a few concise tables. In addition, some of the properties (especially mechanical properties) have different values in different tables! The tables in this article began as an attempt to gather a working data set of materials properties for my own work and contain data from a plethora of sources (including some unpublished data and verbal communications). When these sources disagree significantly on a property value, an educated estimate has been made.

The two basic uses for transparent materials in IR sampling are as windows and as attenuated total reflectance

(ATR) elements. In both types of applications, the edges of the optical material itself commonly function as the optical element's means of registration and mounting. Because of the varied limitations of IR-transmitting materials, mid-IR design choices are often complex and difficult. The materials themselves cover a diverse gamut, including some that are seriously toxic, frightfully expensive, or amusingly exotic. The approach in this article is first to introduce the general types of materials, then explore the optical, mechanical, thermal, and chemical characteristics relevant to their applications in instrumentation.

2 FAMILIES OF TRANSPARENT MATERIALS

Transparent materials group themselves rather neatly into eight "families" of materials. The colligative characteristic within each family may be chemical, mechanical, optical, or a combination of these. This section introduces these families, and attempts to give a broad-brush description of their salient features.

Table 1 is a list of optical materials with useful mid-IR transparency. It is by no means complete, but rather represents materials I have used or about which I have acquired information. However, this list does include all the materials commonly used in mid-IR practice. In many cases, listed materials are available from multiple manufacturers and their actual properties may vary significantly. In particular, some of the materials are sold both as single-crystalline materials and as polycrystalline or amorphous materials. I have tried to include some tradenames both as a way of further identifying materials and as an aid to locating the rarer materials.

Table 1. Families and names of transmissive optical materials.^a

Family	Material	Other names	Symbol
Alkali metal halides (salts)	Sodium chloride	Rocksalt, halite	NaCl
	Potassium chloride	Sylvite	KCl
	Potassium bromide		KBr
	Cesium bromide	Cæsium bromide	CsBr
	Cesium iodide	Cæsium iodide	CsI
Metal fluorides	Lithium fluoride		LiF
	Magnesium fluoride	Sellaite, Irtran-1	MgF ₂
	Calcium fluoride	Fluorspar, fluorite, Irtran-3	CaF ₂
	Strontium fluoride		SrF ₂
	Barium fluoride		BaF ₂
Heavy metal halides	Silver chloride	Cerargyrite, chlorargyrite, hornsilver	AgCl
	Silver bromide	Bromyrite	AgBr
	Thallium bromochloride	KRS-6, Tl(Br,Cl), TlBr _{0.4} Cl _{0.6}	KRS-6
	Thallium bromoiodide	KRS-5, Tl(Br,I), TlBr _{0.42} I _{0.58}	KRS-5
Metal oxides	Magnesium oxide	Irtran-5, crystalline magnesia	MgO
	Sapphire	α -Alumina, sapphire, corundum	α -Al ₂ O ₃
	Crystal quartz	α -Quartz, rock crystal, silicon dioxide	α -SiO ₂
	Zirconia	Cubic zirconia (Hf-doped)	ZrO ₂
II–VI chalcogenides	Zinc sulfide	β -ZnS, sphalerite, Irtran-2, Cleartran	ZnS
	Zinc selenide	Irtran-4	ZnSe
	Cadmium sulfide	Greenockite	CdS
	Cadmium selenide	Cadmoselite	CdSe
	Cadmium telluride	Irtran-6	CdTe
Groups IV and III–V	Diamond	(Type IIa)	C
	Silicon	FZ-Si (undoped vacuum-grown float-zone)	Si
	Germanium		Ge
	Gallium arsenide		GaAs
Glasses	Silica glasses	Fused quartz, vitreous quartz, Vycor	vSiO ₂
	Borosilicate glasses	Pyrex, BK-7, LEBG	BSCG
	Fluorozirconate glass	ZBLAN, HMFG	HMFG
	Arsenic trisulfide glass	Orpiment glass	As ₂ S ₃
	AMTIR-1	Ge ₃₃ As ₁₂ Se ₅₅ glass	AMTIR
Plastics	Polyethylene	(Usually, high-density) poly, polythene	HDPE
	Polymethylpentene	TPX, PMP	TPX
	Polyester	PET, PETG, Mylar, Melinex	PET
	Polytetrafluoroethylene	Teflon TFE, PTFE	PTFE
	Fluorinated EPC	Teflon FEP, TFE/HFP	FEPC

^aNames were selected on the basis of their descriptive value and common use; the names in parentheses include the commonest tradenames. Owing to space limitations, many material names are vulgar: some “proper” names such as poly(4-methylpent-1-ene) and poly(ethylene terephthalate) have been truncated, and lengthy designations such as fluorinated ethylene–propylene copolymer (EPC) and tetrafluoroethylene–hexafluoropropylene copolymer have been omitted. Symbols are for convenience; they are mostly chemical formulas but also include some common designators for nonstoichiometric materials. Trademarks include Kodak’s Irtran, Amorphous Materials’ AMTIR, CVD’s Cleartran, Corning’s Pyrex and Vycor, Mitsui’s TPX, and Dupont’s Teflon, Melinex, and Mylar.

2.1 Soluble halides

Sodium chloride (table salt, NaCl) is the paragon of this family, composed of the I–VII salts (except fluorides). The members of this family are of gratifyingly low refractive index (RI), but are notably water-soluble, soft, and relatively weak. The pioneering work in the mid-IR region was accomplished with NaCl optics. The modern low-wavenumber limit of the mid-IR region (400 cm^{−1} or

25 μ m) was originally defined by the transmission limit of thick KBr optics. This family of materials has unrealized potential: practitioners who only consider the commonly used ones (NaCl, KBr, and CsI) ignore the least hygroscopic member, the versatile and inexpensive KCl. They neglect the robust CsBr, which is as hard as KBr, but does not cleave and is notably resistant to shock and point stress. Also neglected are the inexpensive (but difficult to find) polycrystalline NaCl and KCl, which combine superior

strength (quadruple the practical strength of the crystalline materials!) with freedom from cleavage. CsI is a workhorse in the far-IR region, but in the mid-IR region it is inferior to its cousins, being fingernail-soft and extremely hygroscopic.

2.2 Fluorides

Calcium fluoride (fluorspar, CaF_2) is the paragon of this family, characterized by low water solubility and low RI. Calcium fluoride is often used for aqueous transmission cells because it resists corrosion by water. Barium fluoride is slowly etched by water, but is sometimes used for aqueous transmission measurements because its useful spectral range includes the major low-absorptivity spectral regions of liquid and frozen water. Solutions containing ammonium ion rapidly corrode most fluorides, and fluorides tend to be sensitive to strong acids. This family (especially BaF_2) has the reputation of being sensitive to thermal shock, although I have personally observed that some (not all!) BaF_2 windows survive immersion in liquid N_2 . A more probable culprit is the deadly combination of thermal shock and transient point stress when windows are constrained in cell mounts.

2.3 Heavy metal halides

The members of this family are the opposite of brittle: they are actually malleable! The silver salts (primarily AgCl and AgBr) are water resistant and transparent over the entire mid-IR range, but they are weak materials prone to cold flow: their flexural apparent elastic limit (FAEL) strength must be derated at least 25-fold in long-term pressure applications! AgCl is sometimes used as an optical solder, or as a crushable index-matching gasket. Contact with metals can initiate rapid electrochemical corrosion; a tidy (but rarely used) solution is to machine the cell body out of silver! AgCl and AgBr photodegrade when exposed to actinic light, preventing their use in monitoring photolytic reactions. AgCl and AgBr are soluble in solutions containing chelating agents, concentrated chlorides, or CN^- , $\text{S}_2\text{O}_3^{2-}$, or Br_3^- ions. Strong oxidizers can strip the halide away from the silver salt, and reducing agents can convert AgCl or AgBr into black deposits of Ag metal.

The thallium salts have outstanding virtues, and KRS-5 has become a ubiquitous optical material in IR practice. Its cousin KRS-6 is rarely used because it is neither harder nor stronger than KRS-5 and has a more limited spectral range. With its transparency and robustness KRS-5 has until recently reigned as the premier material for routine laboratory ATR spectroscopy, and mid-IR optical fibers can be

made from it. After the preceding panegyric, it is important to note that KRS-5 has some severe faults. Thallium is frighteningly toxic; in the USA thallium salts are even banned as rat poison because they are so dangerous! In IR practice, the insolubility of KRS-5 offers considerable protection against accidental poisoning, but polishing operations are hazardous because of the toxicity of the dust. Polish KBr, but leave KRS-5 to the professionals! Another limitation of KRS-5 is its tendency to cold flow, which hampers its use in pressure windows.

2.4 Oxides

These materials (MgO , Al_2O_3 , SiO_2 , and ZrO_2) are in some ways a mixed bag, but they are all hard, tough materials with limited spectral range. Sapphire (clear, crystalline $\alpha\text{-Al}_2\text{O}_3$) is a commonly used (and fairly cheap) material for mid-IR measurements. With its toughness, inertness, and extreme hardness it is a well-deserved favorite for process applications. ZrO_2 probably deserves more attention for ATR applications. Crystalline SiO_2 is rarely used as it has inferior properties (except in the far-IR region) to the ubiquitous fused quartz. MgO in its pressed Irtran-5 form has suffered from incomplete transparency and low strength, but new methods of producing its crystalline form may allow the exploitation of MgO 's superior spectral range.

2.5 II–VI (chalcogenides)

This peculiarly named family of materials includes two workhorses, ZnS and ZnSe . Their use was pioneered with their hot-pressed forms, Irtran-2 and Irtran-4. The advent of CVD (chemical vapor deposited) ZnS and ZnSe has extended their use to ATR applications. Although susceptible to strong oxidizers and aggressive acids and bases, these materials have proved both mechanically and chemically robust in many applications and are favorites for process IR spectroscopy. Although zinc, sulfur, and selenium are all vital nutrients, both materials can be hazardous. Selenium is toxic in remarkably small doses, and zinc-containing dusts are legendarily allergenic. Cadmium telluride is occasionally used for similar applications, but it is fragile, toxic, and chemically vulnerable. Note that the chalcogenide glasses (e.g. AMTIR and orpiment glass) are grouped with the glasses in Section 2.7, not here.

2.6 IV and III–V (diamond family)

This group contains some of the most unique and useful IR-transmitting materials which exist, all of them extremely

hard and brittle, but impervious to thermal shock because of their low expansion coefficients and high thermal conductivities. Diamond is certainly the most expensive IR optical material in common use. Type IIa diamonds are generally used because of their superior IR transmission, which covers the whole mid-IR range except for a phonon band around 2000 cm^{-1} ($5\text{ }\mu\text{m}$). Diamond is the premier material for high-pressure cells, although great care has to be taken to avoid failure by crystal plane cleavage. Note that although properly oriented and mounted diamonds achieve a strength of 8700 MPa, a more realistic strength figure for ordinary mounting is a mere 370 MPa! Inexpensive thin plates of synthetic diamond, produced by vapor deposition, have now become available. Silicon is the little cousin of diamond, and a very inexpensive material because of the semiconductor industry. In practical window thicknesses, Si transmits light over the entire mid-IR range except for a narrow two-phonon band at 610 cm^{-1} ($16.4\text{ }\mu\text{m}$). Note that undoped vacuum-grown float-zone material should be used; the more common Czochralski-grown Si has significant absorptions from C and O impurities, including a broad band at 1100 cm^{-1} ($9.1\text{ }\mu\text{m}$). Ge is a similar material, and even has useful transmission out to 700 cm^{-1} ($\sim 15\text{ }\mu\text{m}$) through a 50-mm thickness of material. Si and Ge both have extremely high refractive indices, useful for ATR measurement at small penetration depths but troublesome for transmission measurements. One caveat: because of free thermal electrons, both Si and Ge become opaque at mildly elevated temperatures. Ge has another undesirable characteristic: Ge coated with Pt or other metals can become irreversibly opaque upon heating in an ordinary laboratory oven. If the facile cleavage of Si and Ge becomes a serious detriment in a particular application, it may be possible to substitute polycrystalline GaAs (which is hard to find but commercially available).

2.7 Glasses

The family of IR glasses includes several materials utilized for IR optical fibers. Opticians may be upset by the short shrift I give the silica glasses (lumping Pyrex and BK-7 together, indeed!), but they are rarely used beyond the near-IR region. The first true mid-IR glass was opium glass, now largely supplanted by ZnSe and AMTIR for discrete optics but being utilized in purer form for fiber optics. AMTIR is utilized for ATR elements when resistance to acidic environments is needed. Fluorozirconate glasses were developed for optical-fiber applications, but are rarely used for discrete optics because CaF_2 is generally superior. Not being stoichiometric materials, glass compositions can be tailored, but such materials belong in the sections on composite and tailored materials.

2.8 Plastics

Several plastics have invaded the unlikely territory of mid-IR optical materials. All of them have significant absorption bands within the mid-IR region but also considerable regions of transparency. Their main uses are as stretched-film environmental windows, specialty-application cell windows, and molded Fresnel lenses. The ease with which they are formed and molded is a major virtue, and their chemical resistances are unique and useful. Although polyethylene cells have been used for far-IR measurements for decades, there are as yet few laboratory mid-IR uses of plastic cells. Chief among these are several schemes utilizing meshes or porous films – surface tension wicks a liquid sample into the pores to form an “oil spot”, volatile solvents evaporate, and the measurement is made in transmission.

3 COMPOSITE MATERIALS

3.1 Coatings

Optical coatings represent the earliest and most ubiquitous examples of tailored materials. MgF_2 antireflection coatings have a long history in visible optics, and they are applied to some mid-IR optics as a way of passivating and hardening the surface. Although MgF_2 has a *reststrahlen* band at $20\text{ }\mu\text{m}$, CaF_2 (with its *reststrahlen* band at $46\text{ }\mu\text{m}$) can be used instead if maximum performance at long wavelengths is needed. The soluble halides are often coated with proprietary organic substances which inhibit fogging. Diamond coatings are not as impervious as the cachet of their name suggests because the pinholes in vapor-deposited diamond coatings can allow moisture to get under the coating and cause it to flake off. Newer diamond coatings perform better because underlayers have been developed which passivate the underlying material and prevent corrosional propagation of defects.

3.2 Tailored materials

An early example of a tailored material is pressed KBr, originally utilized for sample pellets and molded lenses but found useful because of its freedom from cleavage. Polycrystalline (“Polyclear”) NaCl and KCl windows for strength applications are significant improvements over the standard crystalline windows. CVD materials, although originally produced because of the difficulties of growing large crystals of some materials (including ZnS and ZnSe), do exhibit superior properties compared with the natural

materials. Another class of tailored materials is a child of the CVD technique: provided that there is a reasonable match of thermal characteristics, several CVD materials can be deposited in successive layers to form a composite bulk material. With this technique, the superior surface qualities of ZnS can be achieved in an optical element with the superior transmission properties of ZnSe. This kind of tailoring is in its infancy, but holds great promise for creating superior mid-IR optical materials.

3.3 Optical fibers

Although most of the effort spent developing IR optical fibers has been for near-IR communications fibers, significant progress is being made with mid-IR fibers. The good news is that practical mid-IR fibers now exist; the bad news is that none of them transmits light much beyond 1 m in that most important part of the mid-IR region below 2000 cm^{-1} ($>5\text{ }\mu\text{m}$). The premier optical fibers for the region above 2000 cm^{-1} ($<5\text{ }\mu\text{m}$) are fabricated from heavy metal fluoride glasses (e.g. ZBLAN, HMFG). Their integral cladding (an optically thick coating of lower-refractive-index composition) makes them good examples of tailored optical materials, and they are suitable for applications in the 10–20-m distance range. Unfortunately, these fluoride fibers are water-soluble and prey to serious environmental degradation. Presenting a table of mid-IR optical fiber specifications seems foolhardy, since improvement continues and the optical parameters of individual batches still vary very widely.

There are currently a variety of kinds of optical fiber for the $<2000\text{ cm}^{-1}$ ($>5\text{ }\mu\text{m}$) region, but all of them have severe limitations beyond the attenuation which determines their $\sim 1\text{-m}$ length limit. The chalcogenide fibers (e.g. AMTIR and orpiment glass) have reasonable environmental resistance, but are frustratingly brittle and have limited spectral range. Silver halide fibers have reasonable spectral range and may currently hold the length/attenuation record, but are painfully sensitive to light and environmental degradation. KRS-5 fibers are sensitive to environmental degradation, susceptible to scattering losses upon bending, and prey to further losses because they are usually unclad. Many of these fibers have limited numerical aperture (the cone of incident light effectively transmitted down the fiber) because of the limited compositional tailoring developed so far for them. Some high-numerical-aperture fibers (mostly orpiment glass) have been fabricated unclad or by utilizing a polymer sheath in lieu of integral cladding, but these are prey to ATR losses by surface contaminants or by the sheath. All of the $<2000\text{ cm}^{-1}$ ($>5\text{ }\mu\text{m}$ wavelength limit) fibers suffer from serious entrance/exit losses because of their high refractive indices.

In addition to length limits and environmental fragility, a perennial problem for mid-IR optical fibers results from their small diameters. It is simply impossible to cram much light into them with a thermal source, so fiber-based applications tend to be energy-starved. The mid-IR region conspires against optical fibers: materials are brittle, absorbing, and environmentally fragile, sources are weak and detectors are noisy, and the long wavelengths require thick cladding and take their toll with diffraction losses. Hollow optical conduits transmit large energy throughputs and offer other advantages, so they are a more popular method of translocating mid-IR light.

3.4 Matrix materials

A gray area exists with sample diluents. When there is neither solution nor chemical interaction, these diluents are optical materials themselves, as surely as are microscope immersion oils. While the specialized index-matching oils such as are used for optical fibers are outside the scope of this article, I should at least mention some common examples of these diluent matrices, which admirably fulfill a variety of dispersion and index-matching roles. Many of these matrices are also used in bulk form as conventional optical materials, and appear in the tables.

One of the earliest sampling methods was the KBr pellet, consisting of the sample dispersed and finely ground within a KBr matrix which was then cold-pressed into a transparent disk. A lesser-known version using powdered polyethylene was tedious to make because of triboelectrically generated repulsion (unless manipulated in a radioactive environment!). Another hoary but ubiquitous and effective sampling method utilizes a mortar-and-pestle mull of the sample in alkane oil (mineral oil, Nujol), pressed between KBr plates. A perfluoroalkane oil (perfluorokerosene, Fluorolube) mull allows spectral coverage in the regions obscured by the alkane oil's few absorption bands. For reference, the spectra of these mulling oils are shown in Figure 1.

Diffuse reflection spectroscopy commonly utilizes optically scattering diluent powders, especially KBr, diamond dust, or Si. These diluent powders are vital to the optical nature of the measurement, and reduce the confounding effects of the sample's anomalous dispersion. In a type of combination of gas chromatography with IR spectroscopy, a frozen argon matrix is utilized: the output of the chromatographic column is mixed with argon and "spray-painted" on to a moving cryocooled surface, producing a physical chromatogram consisting of the actual chromatographic eluate striped along a time axis of solid transparent argon. Argon (like the other noble gases) is fairly mid-IR transparent even in solid form, so it serves as a near-perfect matrix for the eluate.

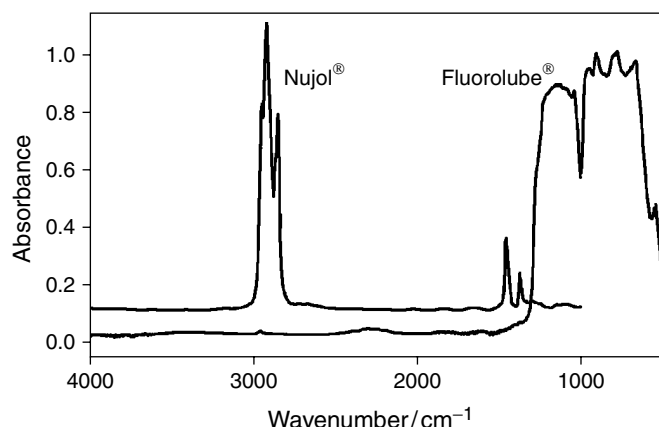


Figure 1. Mid-IR spectra of common mulling agents.

One could argue that IR solvents are also themselves optical materials, since they are commonly utilized as solvent matrices for samples. However, the line must be drawn somewhere, so the liquid chromatographic solvents, excellent supercritical solvents such as Xe and CO₂, and even the traditional (but dangerous) CCl₄ and CS₂, will not be covered in this article.

4 MATERIAL PROPERTIES OF TRANSMISSIVE OPTICAL MATERIALS

4.1 Optical characteristics

Most mid-IR transmissive materials are transparent into the visible or near-IR region on their short-wavelength side, and have a long-wavelength cutoff which defines their useful spectral ranges. A few kinds of materials (e.g. quartz, diamond, silicon, silicate glasses, and plastics) have strong absorption bands within their main spectral range, which produce opaque gaps in their useful transmission range. In Table 2, two long-wavelength cutoff values are listed for each material: one value for typical window thicknesses, and the other value for the long internal pathlengths characteristic of ATR spectroscopy.

In addition to spectral range, the other salient optical property of these materials is their refractive index (RI) (or n). The RI of a particular material is not constant across the entire mid-IR spectral range; the value tends to decrease gradually towards longer wavelength, then decreases more rapidly near the long-wavelength cutoff of the material. This dependence of RI on wavelength is called dispersion. Dispersion is definitely not a constant across the spectral range, but must be considered when prismatic elements or lenses are used in optical systems. Extensive tables and

equations specifying the RI and dispersion of many optical materials throughout their spectral ranges are available in several of the reference books cited at the end of this article. Nevertheless, the RI value of a material is reasonably constant across the mid-IR range, so for the purposes of this article a single value of RI is given for each optical material in Table 2.

RI affects three important elements of mid-IR measurements. First, reflection within a window or a cell can produce interference fringing which appears as a sinusoidal addition to the spectrum. Organic liquid measurements are particularly susceptible to these troublesome fringes because liquid transmission cells are often in the millimeter to submillimeter thickness range. Because organic liquids commonly have refractive indices around 1.5 (usually ± 0.2 RI units), low-index optical materials are valued as trouble-free windows for liquid cells, since a near-match in RI between the liquid and the window (a low Δn) suppresses the intensity of interference fringing. Interference fringing can also be suppressed by wedging the cell volume, or by choosing resolution–thickness combinations which avoid fringing (e.g. 8 cm⁻¹ resolution with a 1-mm cell, or second-derivative spectroscopy with thin cells).

Reflectance at a single surface (between two nonabsorbing media with RIs, n_1 and n_2) is described by

$$R = \left[\frac{(n_2 - n_1)}{(n_2 + n_1)} \right]^2$$

Note that n_1 is often represented by air, $n = 1.0$.

Second, reflection losses are high whenever light traverses a large step change in RI. These are often termed “window losses”, and a series of high-RI windows can eat up much of a spectrometer’s beam intensity while spraying reflected light into inconvenient places inside the instrument. Although broadband mid-IR antireflection coatings are available, they are expensive and sometimes of dubious mechanical/chemical durability.

Third, materials of high RI are necessary for ATR spectroscopy, a valuable technique for the measurement of many difficult liquid and solid samples. The technique requires that Δn (the ATR element’s RI minus the sample’s RI) be high enough to provide a conveniently wide range of supercritical angles, since the technique requires that the sample contact the surface where total internal reflection of the IR light is taking place. As will be described in other articles, the ATR interaction with the sample effectively “penetrates” only a fraction of the light’s wavelength. With very high-RI ATR elements, the reflection angle can conveniently be far in excess of the critical angle, resulting in an even smaller effective sample “penetration” depth. Since the “penetration” depth varies with wavelength

Table 2. Optical characteristics of transmissive optical materials.^a

Material	Symbol	Refractive index, $n_{5\mu\text{m}}$	Long-wavelength limit (μm)		Comments
			$T_{<6\text{ mm}}$	$T_{50\text{ mm}}$	
Sodium chloride	NaCl	1.52	18	15	
Potassium chloride	KCl	1.47	23	19	
Potassium bromide	KBr	1.54	30	25	
Cesium bromide	CsBr	1.66	42	38	
Cesium iodide	CsI	1.74	60	48	Easy to scratch
Lithium fluoride	LiF	1.33	7	6	
Magnesium fluoride	MgF ₂	1.34	8	6.5	Birefringent
Calcium fluoride	CaF ₂	1.40	10	8.5	
Strontium fluoride	SrF ₂	1.41	11.5	10	
Barium fluoride	BaF ₂	1.45	12	11	
Silver chloride	AgCl	2.00	27	21	Darkened by UV
Silver bromide	AgBr	~2.15	34	30	Darkened by UV
Thallium bromochloride	KRS-6	2.19	25	21	
Thallium bromoiodide	KRS-5	2.38	45	40	Orange-red
Magnesium oxide	MgO	1.64	8	6	Birefringent
Sapphire	α -Al ₂ O ₃	1.62	6	4	Birefringent
Crystal quartz	α -SiO ₂	1.47/4 μm	4	2.6	Birefringent
Zirconia	ZrO ₂	2.13/0.5 μm	5.5	5	
Zinc sulfide	ZnS	2.25	14	10.5	
Zinc selenide	ZnSe	2.43	20	15	Yellow
Cadmium sulfide	CdS	2.24	15	12	Birefringent
Cadmium selenide	CdSe	2.45	20	15	Visually opaque, birefringent
Cadmium telluride	CdTe	2.70	28	~20	Visually opaque
Diamond	C	2.39	80	N/A	
Silicon	Si	3.42	50	8.5	Visually opaque
Germanium	Ge	4.02	23	14	Visually opaque
Gallium arsenide	GaAs	3.82	17	12	Visually opaque
Silica glasses	vSiO ₂	1.404 μm	4	2.6	OH absorption varies
Borosilicate glasses	BSCG	1.502 μm	2.5	2	Strong OH absorption
Fluorozirconate glass	HMFG	1.50/0.5 μm	8	6.5	Little OH absorption
Arsenic trisulfide glass	As ₂ S ₃	2.41	13	~8	
AMTIR-1	AMTIR	2.51	16	11.5	Visually opaque
Polyethylene	HDPE	1.54	d	–	Visually translucent
Polymethylpentene	TPX	1.43	d	–	Visually transparent
Polyester	PET	~1.54/0.5 μm	d	–	Visually transparent
Polytetrafluoroethylene	PTFE	1.35/0.5 μm	d	–	Visually translucent/opaque
Fluorinated EPC	FEPC	1.34/0.5 μm	d	–	Visually transparent/translucent

^aRefractive index values are given for room temperature and 5 μm wavelength, except as noted. Approximate wavelength limits are given for two material thicknesses, <6 mm and ~50 mm. Wavelength limits designated 'd' (discontinuous) indicate interrupted regions of transparency. Diamond has a narrow absorption band at 5 μm . Silicon has a narrow 2-phonon absorption band at 16.4 μm . Czochralski-grown silicon has an additional absorption band due to oxygen at 9 μm . Semiconductors (e.g. Si, Ge, CdTe, GaAs) display free-carrier absorption at elevated temperatures, limiting their use at high temperatures.

and with the (nonconstant) Δn , the effective ATR sampling depth varies severalfold across the mid-IR spectral range.

Several other optical properties affect specific kinds of measurements. Some of the materials are birefringent, which means that the material has different RI values depending on polarization of the light beam through the crystal. Table 2 presents “in-between” RI values for such

materials, since many of these crystalline materials are cut at special angles in order to minimize birefringence when used as windows. The RI of a material may also vary with pressure and electrical charge, allowing the construction of photoelastic polarization modulators and acousto-optically scanned monochromators. However, these are very specialized applications of mid-IR optical materials and beyond the scope of this article.

Table 3. Mechanical properties of transmissive optical materials.^a

Material	Symbol	Strength, <i>Fa</i> (MPa)	Fracture toughness (MPa m ^{1/2})	Hardness (Knoop) (kgf mm ⁻²)	Density, <i>D</i> (g cm ⁻³)	Comments
Sodium chloride	NaCl	2.4 (9.5)	?	18	2.16	Cleaves
Potassium chloride	KCl	2.2 (11)	?	17	1.98	Least hygroscopic salt, cleaves
Potassium bromide	KBr	1.1	?	7	2.75	Cleaves
Cesium bromide	CsBr	8.3	?	20	4.44	Shock resistant, does not cleave
Cesium iodide	CsI	2.7 (5.6)	?	20	4.53	Shock resistant, deforms (cold flow)
Lithium fluoride	LiF	11	?	99	2.64	Sensitive to thermal shock, cleaves
Magnesium fluoride	MgF ₂	49	1.0	415 (575)	3.18	Rugged, cleaves
Calcium fluoride	CaF ₂	37 (54)	0.5	158	3.18	Hard, fairly tough
Strontium fluoride	SrF ₂	~35	?	154	4.28	
Barium fluoride	BaF ₂	27	?	82	4.88	Sensitive to mechanical shock
Silver chloride	AgCl	26 (<1)	?	10	5.56	Deforms (cold flow)
Silver bromide	AgBr	~30 (1.1)	?	7	6.47	Deforms (cold flow)
Thallium bromochloride	KRS-6	21	?	39	7.19	Deforms (cold flow), dust very toxic
Thallium bromiodide	KRS-5	26	?	40	7.37	Deforms (cold flow), dust very toxic
Magnesium oxide	MgO	27	?	692	3.58	Tough
Sapphire	α-Al ₂ O ₃	448 (689)	3.0	1370	3.98	Very hard, tough
Crystal quartz	α-SiO ₂	~41	?	820	2.65	Brittle, inert, cleaves
Zirconia	ZrO ₂	?	2.0	~1160	5.85	
Zinc sulfide	ZnS	60 (103)	0.5 (0.8)	160 (250)	4.09	Tough, dust allergenic
Zinc selenide	ZnSe	55	0.33	120	5.27	Fairly tough, dust allergenic
Cadmium sulfide	CdS	28	?	108	4.82	Birefringent, dust toxic
Cadmium selenide	CdSe	?	?	~70	5.67	Brittle, birefringent, dust toxic
Cadmium telluride	CdTe	~6	?	56	5.85	Very brittle, dust toxic, visually opaque
Diamond	C	370 (8700)	2.0	8820	3.52	Very hard and inert, cleaves
Silicon	Si	~62	0.95	1150	2.33	Very hard and inert, visually opaque
Germanium	Ge	~49	0.66	780	5.33	Very brittle, visually opaque
Gallium arsenide	GaAs	~50	?	721	5.32	Dust toxic
Silica glasses	vSiO ₂	~35	0.8	461	2.20	
Borosilicate glasses	BSCG	~35	?	~500	2.35	
Fluorozirconate glass	HMFG	~25	?	225	4.33	Sensitive to thermal shock
Arsenic trisulfide glass	As ₂ S ₃	~8	?	109	3.20	Brittle, dust toxic
AMTIR-1	AMTIR	~18	?	170	4.40	Brittle, visually opaque, dust toxic
Polyethylene	HDPE	27	?	R60	0.95	LDPE deforms (hardness only R15)
Polymethylpentene	TPX	~24	?	R60	0.83	Fairly rigid
Polyester	PET	~98	?	R110	1.37	Strong, e.g. stretched-film windows
Polytetrafluoroethylene	PTFE	~22	?	R58	2.24	Deforms (cold flow), visually opaque
Fluorinated EPC	FEPC	~18	?	R25	2.15	Deforms (cold flow)

^aStrength (*Fa*) is defined as the elastic limit or flexural apparent elastic limit. Crystalline strength is often limited by brittleness and cleavage; higher effective strength can often be achieved by careful orientation and mounting. Parenthetical *Fa* values for CaF₂, NaCl, KCl, and ZnS are for polycrystalline materials. Parenthetical *Fa* value for CsI is for work-hardened material. Parenthetical *Fa* values for AgCl and AgBr are empirical “strengths” for long-term pressure applications where cold flow is the determining factor. The low *Fa* value for diamond reflects its brittleness and easy cleavage; the parenthetical value is achieved by careful orientation and mounting. Fracture toughness measures the difficulty of propagating an incipient fracture. Fracture toughness value for ZnS is for the crystalline material; the parenthetical value is for CVD material. Parenthetical hardness values for MgF₂ and ZnS are for hot-pressed materials (e.g. Irtran). Hardness values for plastic resins are in Rockwell units.

4.2 Mechanical characteristics

The published mechanical characteristics of optical materials are surprisingly fragmentary and contradictory. The gleaning of the data for Table 3 was by far the most difficult part of my data-gathering effort, and these mechanical data are still the most approximate and suspect of all the

optical materials properties presented in this article. In addition to the inexactitude of the numbers, their application is fraught with twists and turns. Note the two strength values for diamond: they differ by 24-fold, even though they describe the same material! The subtleties of point stresses and incipient cracks mock attempts to “design by the numbers” alone.

The first mechanical property goes by the somewhat misleading title of “strength”. It is an appropriate designation as long as the stories of Achilles, Icarus, and Varus are kept firmly in mind! For materials subject to sudden failure, the load at the elastic limit is Fa , but for many materials incipient failure is heralded by an increase in the load versus deformation and Fa is then defined as the “flexural apparent elastic limit” (FAEL), the point where $\delta_{\text{deformation}}/\delta_{\text{load}}$ increases by 50%. No distinction between these definitions is made in the table.

For well-behaved materials, circular pressure windows can be designed according to the following equation:

$$Fa = \frac{(SF \times K \times D^2 \times p)}{(4t^2)}$$

where Fa is the strength value for the material, D is the unsupported diameter of the window, t is the thickness of the window, p is the load per unit area (pressure, in megapascals), SF is the safety factor, nominally $SF = 4$, and K is a constant which depends on the mounting method: $K_{\text{clamped}} = 0.75$ or $K_{\text{unclamped}} = 1.125$. To illustrate the design information obtained, this equation can be rewritten as

$$\frac{t}{D} = \left(\frac{SF \times K}{4} \right)^{1/2} \left(\frac{p}{Fa} \right)^{1/2}$$

Windows can either be mounted so that the periphery is constrained flat (clamped), or unconstrained (unclamped). Hard clamping, of course, imposes additional thermal expansion compensation and point stress engineering requirements. This all sounds fairly cut-and-dried, but the reality is that mid-IR optical materials are far from being a well-behaved bunch! The equations are included only to illustrate the interrelationships among the mechanical parameters. The flatness, scratch and dig, and deburring of contact surfaces are of paramount importance in maintaining window strength. Much more than a few data tables is needed to design a cell, unless it is for a low-pressure, room-temperature, low-toxicity application where neither life nor property would be imperiled by catastrophic cell failure.

Fracture toughness is the second mechanical property listed. It could be the most predictive mechanical property, since it addresses a very common (perhaps the most common) failure mechanism for mounted transmissive optical elements. Unfortunately, fracture toughness values are unavailable for the majority of transmissive optical materials. The extremely high point stresses generated in very hard materials conspire with low fracture toughness to create what we might characterize as “brittleness”. This combination of properties is a good explanation for the legendary brittleness of diamond, and the comparative toughness of sapphire or fused silica.

As indicated above, hardness is a liability in many applications of transmissive optical materials. Hard things shatter. However, hardness also has its virtues. In applications where contact with solid samples is necessary, harder materials last longer without dulling or scratching. Even where the problem is only rough handling, hard windows such as ZnSe (which is hard compared with “full-range” materials such as KRS-5 or KBr) and sapphire (very hard!) are popular. The ascendancy of single-application instruments has crystallized efforts to find durable optics for particular applications. A solution to this dilemma is slowly being found in tailored materials, which (like Damascus steel or a fine *nihontō*) manage to be hard and tough at the same time.

4.3 Thermal characteristics

The thermal characteristics of common window materials are presented in Table 4. Thermal conductivity becomes important when large temperature gradients or temperature shifts are part of the engineering lifetime of an optical element. The premier family of high-thermal-conductivity windows is diamond and its relatives Si, Ge, and GaAs, although MgO, sapphire, and ZnS also have notably high thermal conductivities.

Thermal expansion, in addition to its potentiating effect in translating $\delta T/\delta t$ into destruction, is a parameter which must be honored in any cell design for high or low temperatures. Cell optics must survive repeated transitions to and from room temperature. When low pressures are involved and unconstrained (or spring-mounted) optics are practical, cell design can remain primitive and effective. However, when pressure requirements necessitate that the optics be constrained and temperature excursions are necessary, thermal compensation must be considered. KBr's expansion coefficient is quadruple that of Hastelloy C! The diamond family (C, Si, Ge, and GaAs) have very low thermal expansion coefficients, and CaF_2 , BaF_2 , and HMFG are blessed with thermal expansion coefficients similar to that of 316 stainless steel.

The maximum-use temperatures are based partly on defined physical properties and partly on spectroscopic folk wisdom. Certainly KBr is not rated anywhere near its melting point of 734°C , but extended service at 300°C does etch its surface! Diamond does not self-destruct anywhere near its rated temperature, but it does burn in air. An interesting group of optical materials are the semiconductors (e.g. Si, Ge, GaAs, CdTe), where free carrier absorption prohibits their use as transmissive optical materials at high temperatures. In essence, at high temperatures these materials become too electrically conductive to transmit light. An additional caveat for these materials (especially germanium)

Table 4. Thermal properties of transmissive optical materials.^a

Material	Symbol	Thermal conductivity (mW cm ⁻¹ K ⁻¹)	Thermal expansion (10 ⁻⁶ K ⁻¹)	Maximum use temperature (°C)	Comments
Sodium chloride	NaCl	65	44	400	Slightly sensitive to thermal shock
Potassium chloride	KCl	65	36	400	
Potassium bromide	KBr	48	43	300	
Cesium bromide	CsBr	10	48	400	Sensitive to thermal shock
Cesium iodide	CsI	11	50	200	
Lithium fluoride	LiF	40	37	400	Very sensitive to thermal shock
Magnesium fluoride	MgF ₂	~150	11	500	
Calcium fluoride	CaF ₂	97	19	600	
Strontium fluoride	SrF ₂	83	18	~600	Sensitive to thermal shock
Barium fluoride	BaF ₂	117	18	500	
Silver chloride	AgCl	11	30	200	
Silver bromide	AgBr	6	30	200	
Thallium bromochloride	KRS-6	7	51	200	
Thallium bromiodide	KRS-5	5	60	200	
Magnesium oxide	MgO	435	12	>2000	
Sapphire	α-Al ₂ O ₃	240	8.4	1700	
Crystal quartz	α-SiO ₂	12	11	>1200	
Zirconia	ZrO ₂	~19	~9	>1000	
Zinc sulfide	ZnS	272	6.4	300	
Zinc selenide	ZnSe	180	7.3	300	
Cadmium sulfide	CdS	159	4.6	~200	
Cadmium selenide	CdSe	?	4.9	>200	
Cadmium telluride	CdTe	63	4.5	300	
Diamond	C	23 200	0.8	>700	Opaque at high temperatures
Silicon	Si	1490	4.2	300	
Germanium	Ge	602	6	100	
Gallium arsenide	GaAs	523	~4.5	~200	Opaque at moderate temperatures
Silica glasses	vSiO ₂	14	0.6	1070	
Borosilicate glasses	BSCG	~11	~3.2	500	
Fluorozirconate glass	HMFG	6.3	17	150	Sensitive to thermal shock
Arsenic trisulfide glass	As ₂ S ₃	2	25	~150	
AMTIR-1	AMTIR	2.5	12	300	
Polyethylene	HDPE	5	120	120	Softens
Polymethylpentene	TPX	1.7	117	160	
Polyester	PET	2.4	80	~120	
Polytetrafluoroethylene	PTFE	2.5	100	250	Phase change at ~76 °C
Fluorinated EPC	FEPC	2.5	95	250	

^aMaximum use temperatures for semiconductors (e.g. Si, Ge, CdTe, GaAs) are far below maximum survival temperatures. Their low maximum use temperatures are due to thermally generated free-carrier absorption and so are thickness dependent. High-temperature chemical interactions with samples and window mounting materials can be a serious materials problem. PET undergoes a phase change which can be utilized for tightening stretched-film windows with a heat gun.

is that thin metal coatings may diffuse into the bulk material at ordinary laboratory-oven temperatures, rendering the optical element permanently opaque.

4.4 Chemical resistance

Transmissive optical elements must be chosen for resistance to the chemical environment. Humidity is a traditional enemy of mid-IR optics, and the alkali metal halides can

be irretrievably etched by momentary exposure to condensing moisture. The water solubilities listed in Table 5 show why. Materials with low solubilities (e.g. BaF₂) are generally resistant to this “fogging” effect, but are slowly etched by flowing liquid water. Such etching rapidly accelerates if certain kinds of complexing agents are present (NH₄⁺ is a nemesis to BaF₂ and CaF₂). A list of common chemical incompatibilities is included in Table 5 as a guide, but be warned that this list is nowhere near inclusive. Also, in

Table 5. Chemical properties of transmissive optical materials.^a

Material	Symbol	Solubility in H ₂ O (satd wt%)	Incompatibilities	Comments
Sodium chloride	NaCl	26.5	Water, glycols, high humidity	Inexpensive
Potassium chloride	KCl	25.8	Water, alcohols, ether, wet solvents	Inexpensive
Potassium bromide	KBr	39.5	Water, alcohols, ether, humidity	
Cesium bromide	CsBr	55.4	Water, alcohols, humidity	
Cesium iodide	CsI	61.5	Water, alcohols, any humidity	
Lithium fluoride	LiF	0.27	Water, HF	
Magnesium fluoride	MgF ₂	0.0076	Conc. acids	Rugged
Calcium fluoride	CaF ₂	0.0015	Ammonium ion, some conc. acids	Fairly tough
Strontium fluoride	SrF ₂	0.012	Ammonium ion, hot HCl	
Barium fluoride	BaF ₂	0.16	Ammonium ion, acids	
Silver chloride	AgCl	0.00014	Oxidizers, chelators, conc. chloride	Attacks base metals, UV darkens
Silver bromide	AgBr	0.00001	Oxidizers, chelators, conc. chloride	Attacks base metals, UV darkens
Thallium bromochloride	KRS-6	0.3	Methanol, chelators, strong bases	Dust very toxic
Thallium bromoiodide	KRS-5	0.05	Methanol, chelators, strong bases	Dust very toxic
Magnesium oxide	MgO	0.00062	Conc. acids, ammonium ion	
Sapphire	α -Al ₂ O ₃	Insol.	Conc. acids and bases	Inert
Crystal quartz	α -SiO ₂	Insol.	HF, some hot conc. bases	Inert
Zirconia	ZrO ₂	Insol.	HF, H ₂ SO ₄	Fairly inert
Zinc sulfide	ZnS	0.00069	Strong oxidizers, some acids	Dust allergenic
Zinc selenide	ZnSe	<0.001	Acids, strong conc. bases	Dust allergenic
Cadmium sulfide	CdS	0.00013	Acids	Dust toxic
Cadmium selenide	CdSe	Insol.	Acids	Dust toxic
Cadmium telluride	CdTe	Insol.	Oxidizers, some acids	Dust toxic
Diamond	C	Insol.	K ₂ Cr ₂ O ₇ + conc. H ₂ SO ₄	Expensive, very inert
Silicon	Si	Insol.	HF + HNO ₃	Inexpensive, very inert
Germanium	Ge	Insol.	Hot H ₂ SO ₄ , aqua regia	Some interaction with redox agents
Gallium arsenide	GaAs	Insol.	Acids, strong oxidizers	Dust toxic
Silica glasses	vSiO ₂	Insol.	HF, strong bases	Inert
Borosilicate glasses	BSCG	Insol.	HF, strong bases	Inert
Fluorozirconate glass	HMFG	>1	Water, high humidity	
Arsenic trisulfide glass	As ₂ S ₃	0.00005	Alcohols, bases	Dust toxic
AMTIR-1	AMTIR	Insol.	Bases	Dust toxic
Polyethylene	HDPE	Insol.	Hot organics, oxidizing acids	Inexpensive
Polymethylpentene	TPX	Insol.	Chlorinated aromatics	Inexpensive
Polyester	PET	Insol.	Halohydrocarbons	Inexpensive
Polytetrafluoroethylene	PTFE	Insol.	None	Toxic fumes at high temperatures
Fluorinated EPC	FEPC	Insol.	None	Toxic fumes at high temperatures

^aMaterials containing poisonous elements (e.g. Tl, As, Cd, Se) can be handled safely, but dust from grinding or polishing is very hazardous. Chemical incompatibilities often become worse at elevated temperatures; the noted incompatibilities represent interactions at modest temperatures.

the liquid phase, incompatibilities worsen rapidly at higher temperatures. A sometimes-overlooked source of cell corrosion is chemical incompatibility between the optical element and its metal mounting. Some transmissive optical materials (e.g. AgCl and AgBr) are electrochemically active themselves, and many others can provide sources of ions for electrochemically mediated corrosion. Stainless steel is not always corrosion free!

Aerosols pose a serious “fogging” danger to mid-IR windows exposed to the environment or to gaseous sample

streams. In many cases, hygroscopic particulates (e.g. SO₄²⁻, salt) are present which form highly corrosive aerosols with even modest humidity. Once an aerosol is present, acid gases which are otherwise benign to transmissive materials can become powerful corrosive agents by dissolving in the aerosol particles. For this reason, corrosion via particulates can sometimes be suppressed by elevating the temperature so that the particulates are no longer hydrous. Centrifugal or media filtration should normally be employed when particulates are a problem.

Among the comments in Table 5 are indications of extraordinary toxicity. Many of the materials listed are somewhat toxic and should be handled with care, but it would not serve the expected readership simply to label everything “toxic”. Therefore, only materials easily capable of poisoning unwary spectroscopists are listed as toxic. Overall, most bulk optical materials are reasonably safe to handle (given minor prophylaxis such as hand-washing or gloves), but several can become dangerous or deadly during ill-advised grinding and polishing operations.

5 REFLECTIVE MATERIALS

Reflective optics are an important, often essential, part of mid-IR optical systems. Unlike transmissive optics, reflective optics are usually composite materials: the reflecting surface is rarely the same composition as the bulk material. Typically, a reflective optical element consists of the actual reflecting surface bonded to a plate, block, or assembly which provides a means of registration and mounting.

Reflective optical elements generally have a surface which is either flat, spherical, elliptical, parabolic, or toroidal. Toroidal mirrors are now mostly historical artifacts, a way to approximate an elliptical surface with a non-computer-driven diamond lathe, but they are sometimes still used when ellipses with equidistant focal points are needed. Most curved mirrors are concave (except for the convex mirror used as part of Cassegranian telescopes). Although on-axis optics (such as Cassegranians and source spheres) are often utilized, most of the reflecting optics in mid-IR instrumentation are off-axis. The design freedom allowed by inexpensive diamond machining has revolutionized mid-IR optical design.

Reflective optics have the advantage of intrinsic achromaticity. There is no wavelength-dependent focus shift,

although differential reflectance effects can produce mild polarization and beam coloration in off-axis optics. Metals are generally used for reflecting surfaces, and many metals have very good reflection in the mid-IR region. However, metal reflection is inevitably lossy, unlike dielectric reflection. Dielectric-enhanced metal surfaces have limited use in general mid-IR instrumentation because of the broad wavelength range involved, and because it is difficult to produce adherent coatings with the thicknesses required at long wavelength. Broad-range dielectric reflectors do find use as interferometric beamsplitters in Fourier transform infrared (FT-IR) instrumentation, and Fabry–Perot dielectric filters are extensively used in nondispersive infrared (NDIR) instrumentation.

The metals commonly utilized as reflecting surfaces are shown in Table 6. Normal-angle reflectance at $5\mu\text{m}$ (2000cm^{-1}) gives a good representation of the mid-IR reflectance of these materials. The normal-angle reflectance at the red He–Ne laser wavelength is also given, since red lasers are commonly utilized for alignment of multielement optical systems. Some Knoop hardnesses of these metals are listed; however, vacuum-coated metal surfaces are often much softer than bulk metals. Vapor deposition can be similar to a gentle snowfall: porous, soft, and poorly consolidated. Again, there is a great deal of technique and art in coating metals. In some cases, ion bombardment is used to “hammer down” and harden the metal surface after coating.

In practice, optical coating is an art, rife with recipes and secret techniques. In many cases, there are several underlayers of different materials to assure bonding of the reflective surface to the substrate. In addition, it is common practice to overcoat optics with a very thin dielectric coating (most commonly SiO) in order to provide a harder, more durable surface. Silver is routinely overcoated with MgF_2 to prevent tarnish.

Table 6. Properties of some reflective metals.^a

Metal	Symbol	$R(\perp)$ ($5\mu\text{m}$)	$R(\perp)$ (He–Ne)	n ($5\mu\text{m}$)	k ($5\mu\text{m}$)	Knoop hardness	Chemical reactivities	Comments
Aluminum	Al	0.98	0.90	8.5	46.0	~25, 40	Hg, OH^- , HCl, H_2SO_4	Easy to sputter
Beryllium	Be	0.98	0.54	2.8	21.1	~60, 125	H^+ , OH^-	Stiff, lightweight, poisonous
Chromium	Cr	0.96	0.64	3.2	16.8	935, 1800	H^+ , HCl	Used to bond gold to glass
Copper	Cu	0.99	0.95	3.0	29.6	~40, 163	O_2 , HNO_3 , H^+ , OH^-	Used for heat dissipation
Gold	Au	0.99	0.94	2.7	30.2	30, 45	$\text{O}_2 + \text{Cl}^-$, CN^-	Highest mid-IR reflectance
Molybdenum	Mo	0.99	0.57	3.2	29.1	~600	O_2 , H^+	
Nickel	Ni	0.95	0.64	4.7	18.0	~200, 557	HNO_3 , S, OH^- , H^+	Used for optical conduits
Platinum	Pt	0.95	0.59	5.0	20.0	40, 200	Cl_2 , CN^- , S	Inert
Rhodium	Rh	0.96	0.81	6.8	25.0	~400	H_2SO_4 , H^+	Very hard surface
Silver	Ag	0.99	0.98	3.5	32.0	32, 60	HNO_3 , CN^- , O_3 , H_2S , S	Overcoat needed to avoid tarnish
Tungsten	W	0.98	0.51	2.4	22.5	~820	$\text{HNO}_3 + \text{HF}$, O_2 , H^+	

^a $R(\text{He–Ne})$ refers to reflectivity at $0.633\mu\text{m}$. Reflectivities, n , and k values are at room temperature.

The presence of a thin overcoat or surface contamination fortunately has a much smaller optical effect than might be imagined. Because of the nature of electromagnetic reflection from metals, there is a near-null of the light's electrical field at the metal surface, so surface contamination within a small fraction of the light's wavelength does not result in light absorption, even if the surface contaminant has high absorptivity. Where many reflections occur (e.g. White cells; see **Long Path Gas Cells**), incremental contamination of the reflecting surfaces may have no effect for a long time, but subsequent contamination can result in rapid degradation.

Reflection at grazing angles is a more complicated matter. Approximate optical constants are listed in Table 6. Reflectance at any incidence angle can be calculated using the Fresnel equations with these constants. In general, most metals become less reflective near the grazing angle, and transition metals such as nickel are actually more reflective than gold at certain incidence angles (see **Hollow Optical Conduits for Vibrational Spectroscopy**). Dielectric materials are even more reflective than metals at the grazing angle but have not become popular, perhaps because they may be more susceptible to performance degradation by minor surface contaminants. See **Reflection–Absorption Spectroscopy of Thin Films on Metallic Substrates** for more information about grazing angle reflection.

It should be noted that visible colors do not denote light absorption in the mid-IR region. An infamous example is black anodized aluminum, which is fairly reflective in the mid-IR region! In general, the mid-IR spectra of dyes and pigments do not have the high absorptivities that are characteristic of their visible spectra. The premier light-absorptive material in the mid-IR region is amorphous carbon, and paints containing high loadings of carbon black should be used where low reflectivity is needed.

6 SURFACE FIGURING OF REFLECTIVE OPTICS

One way of classifying optical elements is by the method used to create the optical surface figure. In some cases, the optically figured substrate also functions as the mounting surface, and in other cases, this substrate is rigidly bonded to a mounting surface or block. The most common substrate for reflective optics is aluminum: it is lightweight, easy-to-machine, and a well-known substrate for coatings. Aluminum has few flaws as a substrate for reflective optics; even its fairly high thermal expansion coefficient is usually easy to deal with. Stainless steel is often utilized when reasonable resistance to corrosion is needed. Flat mirrors and spherical mirrors may have

glass substrates if they are produced using float glass or traditional optical grinding/polishing techniques. Other substrates such as ceramics and graphite-filled polymers are not yet widely used, perhaps because aluminum and steel fulfill most requirements.

A description of optical figuring methods follows.

6.1 Traditional lap grinding/polishing

The ancient method of creating an optical figure is by grinding and polishing on a wheel. Flats and spherical surfaces can be made easily, and the technique has even been adapted to produce paraboloids. However, deeply curved optical elements are difficult to produce in this way, and the glass blanks commonly utilized must be accurately bonded to a mounting plate, a difficult step.

6.2 Float glass

Plate glass is often made by floating molten glass on to a liquid tin surface. Glass made by the float technique is usually fairly flat, and mirrors with quarter-wave (visible) surface accuracy can be cut from low-stress float glass. This technique is generally limited to flat surface mirrors, although float-glass segments are used to fabricate cube corners and rotational molding has been used to form concave optics.

6.3 Electroforming

One of the earliest ways to reproduce complex optical surfaces was by electrolytic replication (electroforming). A positive-curvature optical master element (usually either a paraboloid or an ellipsoid) is prepared, then electrolytically coated with nickel. Electroplating is continued until the deposit is thick enough to hold its shape, then the nickel dish is separated from the master and given a final electroplating of rhodium. The resulting parabola or ellipse (usually with a characteristic hole at the axis) is used as a very-low f -number on-axis optical element, or more often cut into a number of off-axis mirrors. These mirrors are then bonded to mounting plates. The optical quality of electroformed mirrors varies widely, and the optical registration of electroformed mirror elements suffers from the uncertainties in the cutting and mounting process.

6.4 Epoxy replication

Once the appropriate optical master element exists, it is possible to produce large quantities of reflective elements

with the desired optical figure from simple materials and crudely machined blanks. The master element is prepared by coating with mold-release agent. A blank is machined with a corresponding surface (e.g. its negative curvature matching the positive curvature of the master), then specialized epoxy is applied and the blank is pushed into close contact with the master. After the epoxy has cured, the blank is released, having now acquired a thin epoxy surface with a precise optical figure. The epoxy-surfaced blank is coated with aluminum to produce the mirror. With reasonably uniform epoxy thicknesses and low-shrink epoxy resins, excellent optical accuracy can be obtained. Since the blank is generally machined complete with mounting surface, the optical and mounting surfaces of the resulting element are accurately registered. Mirrors replicated in this fashion are limited to low-temperature service, but can be fabricated with hard-to-make figures such as inside corners.

6.5 Diamond turning

Precision lathes with diamond bits are now capable of machining surfaces to optical precision. Several blanks are typically mounted on the lathe spindle and machined simultaneously. Often, a final low-tech polishing operation is still needed to polish out the residual striations, which otherwise produce minor but unsightly grating-like dispersion of light. These optics are extensively used in mid-IR process instrumentation because the finished coated optical element contains nothing but metal and is not susceptible to solvent attack or thermal degradation.

6.6 Molding

Although many camera lenses are actually molded, the bulk molding of reflecting elements has not yet become popular for mid-IR instrumentation. Although polymer resins have very high thermal expansion coefficients, moldable glass-filled and graphite-filled polymers are available with very low thermal expansion coefficients.

ABBREVIATIONS AND ACRONYMS

CVD	Chemical Vapor Deposited
FAEL	Flexural Apparent Elastic Limit

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MarkeTech International, single crystals	http://www.mkt-intl.com/single.htm
MaTecK, Material-Tech. & Kristalle	http://www.mateck.de/index.html
Matweb Materials Property Data	http://www.matweb.com/help.htm
Molecular Technology GmbH	http://www.mt-berlin.com/
Multimode fluoride glass fibers	http://thorlabs.com/thorcat/main/2725-000.HTML
NIST Property Data Summaries	http://www.ceramics.nist.gov/srd/summary/advmatdb.htm
Optovac	http://www.optovac.com/
Oriel Instruments Homepage	http://www.oriel.com/tech/curves.htm
Photonics Directory	http://www.laurin.com/Directory/LPHTML/index.htm
Precision optics	http://www.gsilumonics.com/c01optics_frame/about.htm
Princeton Scientific Products	http://www.princetonscientific.com/pages/crystal.html
Principal Metals	http://www.principalmetals.com/utilities/hardness.htm
Remspec Corporation	http://www.remspec.com/
Saphikon Sapphire Products	http://www.saphikon.com/
SEDI Fibres Optiques	http://www.sedi-fibres.com/english/a_somf.html
Spectroscopy Central Ltd.	http://www.spectroscopy.co.uk/irwcom/
SPIE	http://www.spie.org/
TUFTRAN	http://www.cvdmaterials.com/tuftran.htm
TWO-SIX Welcome to II-VI	http://www.ii-vi.com/pages/prod-ii-vi-materials-znse.html
Vidrine's tables	http://www.vidrine.com/stuff.htm
VITRON Spezialwerkstoffe GmbH	http://www.vitron.de/vhpe.shtml