Infrared Optical Materials
and their
Antireflection Coatings

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Preface

Up until the 1940s the branch of science called optics dealt mainly with the ultraviolet and visible parts of the spectrum. The need for optical materials was mostly fulfilled by bulk glass and a few halide crystals. Since that time a new generation of infrared optical systems has been researched and is now being marketed. The developments in infrared lasers and detectors have enabled many laser systems, thermal systems and glass fibre communications systems to be produced. The production of these systems has in turn created a need for infrared optical materials transmitting electromagnetic radiation essentially from the visible out to 14 μm, thus spanning the near middle and part of the far infrared spectrum. Thus materials such as silicon, germanium, gallium arsenide, calcium aluminate glass, chalcogenide glass, zinc sulphide, zinc selenide, the alkali and alkaline earth halides and silicate glass fibres have all been researched and in many cases developed and produced as infrared optical materials during the last 25 years. Most bulk infrared optical materials possess a high refractive index (> 2) and therefore must be antireflection coated. Hence a parallel coatings development has taken place, yielding high efficiency and ultra-durable coatings to a technical standard not thought possible only a few years ago.

Workers have tended to concentrate on a particular area such as fibres, bulk optical materials or antireflection coatings, but many of the problems encountered in the research, development and production of these materials are common, so that these different areas can be thought of as a continuum within one field. Most of the data in this field is scattered in the literature and it is timely that this is gathered together in a single volume, containing a comprehensive reference list to allow the reader to delve more deeply into any particular part of the subject as he or she wishes. The treatment of the subject concentrates more on the optical and general physical properties and the material science aspects of the materials, rather than the solid state physics of them.

It is hoped that this volume, besides providing a useful summary of the state of the art, will enable users to become more familiar with these new infrared optical materials and encourage researchers and producers to

continue to gather data on existing materials and find new ones to fill the very obvious gaps in knowledge which exist at present.

I am indebted to Professor W T Welford for encouraging me to undertake this work and for reading the typescript, to many of my friends and colleagues for direct and indirect help given and finally to my wife Anna and dog Grendel for their patience during the preparation of this volume.

J A Savage
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Introduction

The ability to synthesise materials and use them to perform various functions has been a major factor in human technical progress. For instance the cutting of wood and other vegetation, the breaking of ground and the reaping of sown crops were difficult until the invention of metal tools. The knowledge and use of simple metal synthesis technology allowed such tools to be made, and initiated a great leap forward in man's quality of life. At a much later stage in human progress, the understanding and use of more advanced iron and steel synthesis technology has affected our lives in many obvious ways to the point where iron and steel products are now taken for granted.

We may now be said to be living in a silicon age which may become known as an information technology age. The personal computer and glass fibre cable transmission medium allow many new functions to be performed and many existing ones to be performed more efficiently. Undoubtedly this silicon age will have a major impact on our lives. By now most of us are aware that the microchip has made this possible and that the glass fibre cable using optical carrier waves is able to carry the large quantity of information that microchip systems are able to generate. Thus there is a carrier system available well suited to the task of information exchange on a vast and hitherto uncontemplated scale. Perhaps even now we are beginning to take this technology for granted. But how many of us are aware of the importance of the physics, chemistry, metallurgy, glass and plastics technologies, commonly called materials science, involved in the production of the microchip and the glass fibre? The manufacture of these items, at the heart of current information technology, rests on the ability to synthesise essentially two materials to standards of purity and perfection previously not achieved in our human progress. These materials are the element silicon and the compound silica (SiO_2).

In practice the silicon is doped to control the electrical activity, and dielectrics together with metals are used in creating a microchip. The silica glass fibre composition is adjusted to allow it to perform its waveguiding function by the addition of 10–20% of GeO_2 or P_2O_5. The exacting standards required for the synthesis of Si and SiO_2 to the quality required for

information technology applications are not generally well known. Yet this materials technology is at the beginning of the device and component technology and the subsequent system or consumer product. Countries which recognise the importance of materials technology and are able to exploit it and the devices which spring from it to the full are at the leading edge of technological progress. The struggle, for that is what it is, to achieve the perfection and purity required for device and component use in some cases can require a similar effort to that more familiar to scientists in general of creating a whole system or consumer product. But that struggle offers an opportunity for invention, creativity, involvement and personal satisfaction in what the author has found to be one of the most fascinating fields of human endeavour. The urge to communicate the fascination and primary importance of materials science and technology to others is the motivation for this work on the subject of infrared optical materials and their antireflection coatings.

The manufacture of laser systems e.g. CO_2 (Ream 1982, Hinman and Cannizzo 1983) and thermal systems e.g. thermal imagers (Kuhl 1983) has created the need for bulk 3–5 μm and 8–12 μm infrared optical materials and coatings. Similarly the need for a low loss high information carrying capacity medium has stimulated the development of the low loss optical fibre. In the initial region of the infrared spectrum from 0.75 μm to 14 μm the absorptions of the minor atmospheric constituents, water vapour and carbon dioxide, result in three main 'windows' in the atmosphere (Kruse *et al* 1962); one from 0.75–2.5 μm (near infrared), another from 3.0–5.0 μm (middle infrared) and a third from 7.5–14 μm (far infrared) as shown in figure 1.1. Image intensifiers operate in the near infrared and are able to use
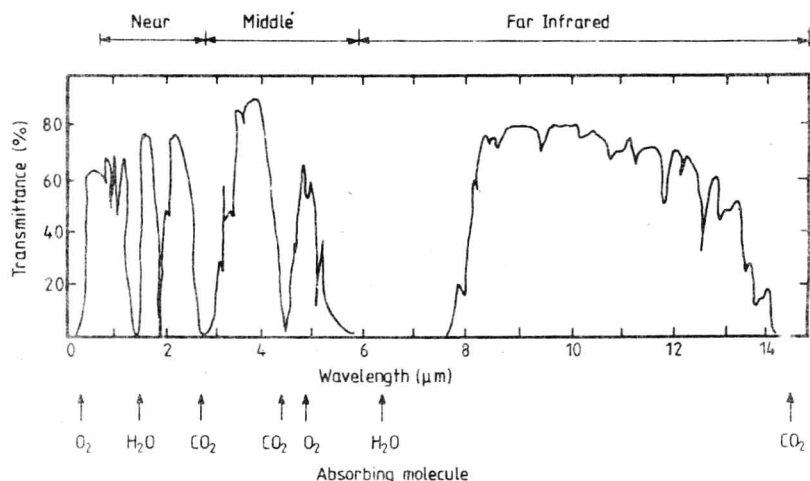
Figure 1.1   Atmospheric transmittance over a 6000 ft sea level path.

existing optical glasses (Kuhl 1983) and do not require specialist new infrared optical materials. From the black body spectral emittance curves shown in figure 1.2 it is clear that to detect relatively hot objects (engine exhausts) the 3–5 μm window is most suitable, and to detect objects at room temperature (human body) the 7.5–14 μm (8–12 μm hereafter) window is most suitable. Thus at present there is a major interest in thermal systems which are concerned with wavelengths up to about 12 μm. In order to process this thermal radiation optically, windows, lenses and telescopes are required. Generally the requirements for infrared transmitting materials are set primarily by the atmospheric transmission and secondarily by the operational wavelength range of the sources and detectors and by the power handling requirements of particular systems. On average, components up to 150 mm in diameter and up to 20 mm in thickness are required but there are occasional needs for much larger ones. In a useful historical review of infrared photography and thermography O'Neill (1983) discusses the industrial, medical and scientific uses of thermal systems. In the case of glass fibres for optical communications the operational wavelengths are in the near infrared, 0.8–1.55 μm, a region close to the optical loss minima in the glasses and at particular wavelengths where semiconducting LED or laser sources are available. Fibres of the order of 50/125 μm core/core plus cladding diameters in lengths of at least 1 km and of low loss (0.5–3 dB km^{-1} depending upon application) are required for optical communications applications. Tebo (1983) discusses the uses of infrared fibres in medicine, optical transfer optics and long distance communications links.
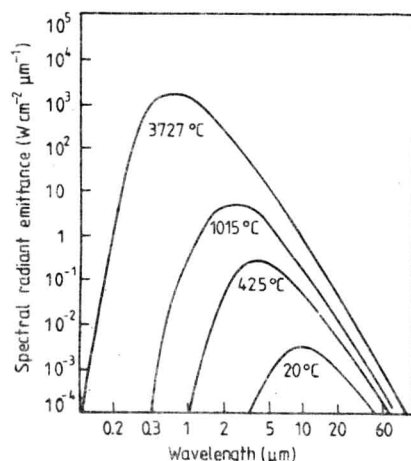
Figure 1.2 Black body spectral emittance curves for a number of temperatures.

The drive to market laser, thermal and fibre optic systems requiring optical components with reproducible properties and reliable performances is establishing the commercial production of infrared optical materials and in some cases new and improved physical measurement techniques for their characterisation. In recent years the technology has been advancing rapidly in the whole field of optical materials, from the ultraviolet to the infrared, as discussed in a review by Musikant (1983). New products are emerging or have emerged in the field of infrared optical materials: spinel ($MgAl_2O_4$), ALON ($5AlN.9Al_2O_3$) and stabilised ZrO_2 for $3-5$ μm use as discussed together with existing materials in Chapter 3; germanium, scaled up GaAs, chalcogenide glass (Ge–[As or Sb]–Se–Te), ZnS, ZnSe, $CaLa_2S_4$, diamond and scaled up alkali halides (KCl, NaCl) for $8-12$ μm and beyond discussed in Chapters 4 and 5; silicate and fluoride optical glass fibres for the near and mid infrared; other halide (Cl, Br, I) and chalcogenide glasses together with crystalline materials (AgCl, AgBr, KRS5) being researched mainly for $8-12$ μm fibre applications as discussed in Chapter 7; a-carbon coating and other amorphous insulators discussed in Chapter 9. Laser damage at wavelengths of 1.06 and 10.6 μm is discussed for some materials in Chapter 6. The development of synthesising and processing techniques such as distillation, vacuum melting, hot isostatic pressing, vapour growth and melt growth including reactive atmosphere processing are discussed in relation to specific materials as appropriate in Chapters 3, 4, 5, 7 and 9. An indication of some of the specialist characterisation techniques such as those for refractive index, MTF, absorption, fracture stress and fracture toughness, thermal shock and rain erosion, necessary for property measurement and quality assessment of infrared optical materials is given in Chapter 8. A diagramatic comparison of transmittance range, refractive index, thermal expansion coefficient, hardness, Young's modulus, rupture modulus and major extrinsic absorption wavelength amongst many infrared optical materials is given in Chapter 2.

2

Loss Mechanisms in Infrared Optical Materials

In solids exhibiting metallic conductivity vacant energy states exist above the Fermi-energy level (the energy level at which 50% of the states are occupied) within the valence band. The uppermost electrons near the Fermi-energy level are the active charge carriers since they can readily occupy these higher energy states or return to the lower energy states when moving in an electric field. These electrons are of such low inertial mass that they can freely respond to electromagnetic radiation over a wide frequency range and thus metals in significant thicknesses are opaque to infrared radiation. In solids where the energy band of the valence electrons is filled and the energy gap between the valence and conduction bands is large (as in the case of insulators), or somewhat smaller (as in the case of semiconductors), electrical conduction and interaction with electromagnetic radiation over a wide frequency range does not readily occur since the electrons are required to 'jump the gap'. Hence only electromagnetic radiation with sufficient energy (short enough wavelength) to enable the electrons to 'jump the gap' interacts with these solids and is absorbed by this electronic mechanism. However, much lower frequency electromagnetic radiation (longer wavelength) is also absorbed by a different mechanism in these insulating and semiconducting materials. This interaction occurs between radiation of mid to very far infrared wavelengths and the vibrational modes of the structural lattice of the materials. Therefore in semiconductors and insulators a transmittance window for electromagnetic radiation exists between the short wavelength absorption cut-off determined by electronic transitions across the band gap and the long wavelength absorption cut-off resulting from interactions with the thermally induced vibrational modes of the structural lattice. It is from these classes of substances that individual materials are selected for use as infrared transmitting elements or windows.

When electromagnetic radiation is incident upon and passes through an insulator or semiconductor, various loss mechanisms operate. Some of the radiation is reflected at the interfaces between the solid and its environment. The amount reflected is determined by the refractive index of the solid and

that of the medium in which it is immersed. This reflection loss is a basic property of the material but may be partially overcome by means of antireflection coatings applied to the surfaces of the solid and this technique is discussed in more detail in Chapter 9. Some of the radiation may be scattered at the surface of the solid and/or in the bulk. The surface scattering is likely to be extrinsic and due to inadequate care in surface preparation. However, bulk scatter can be extrinsic, arising from defects or inclusions, or intrinsic, arising from perturbations in the refractive index, particularly in a complex solid consisting of several atoms of differing masses. Some of the radiation may be absorbed at the surface of the solid or within the solid. Surface absorptions can arise from chemical interactions with the environment leading to the surface extrinsic absorption mechanisms of a similar nature to those in the bulk. The mechanisms which give rise to bulk absorption may be classified as intrinsic or extrinsic ones. The intrinsic absorption mechanisms are those which result in electronic and vibrational lattice absorptions in a crystalline or vitreous material of a specific chemical composition. Extrinsic mechanisms are those associated with impurity atoms or molecules and deviations from stoichiometry. The intrinsic mechanisms define the region of transparency to electromagnetic radiation in a solid and the ultimate transmission achievable within this region, while the extrinsic mechanisms generally determine the percentage of the theoretical level of transparency achievable in practice within this region.

2.1 Intrinsic Absorption

Intrinsic absorption mechanisms in semiconductors and insulators define their region of transparency to infrared radiation. In order to transmit infrared radiation effectively, materials must possess a band gap, E_g, larger than the wavelengths of interest (0.75 to above 12 μm) since it is the band gap that sets the transmittance limit at short wavelengths as seen from figure 2.1. This short wavelength cut-off, λ_c, is defined by the relationship given by (Kruse *et al* 1962)

$$\lambda_c = hc/E_g \qquad (2.1)$$

where h is Planck's constant and c is the velocity of light. The low frequency tail of this short wavelength cut-off extends slightly into the transparent region of a material and is known as the Urbach tail (Urbach 1953, Hopfield 1968) and is of the form

$$\beta \propto e^{cw/kT} \qquad (2.2)$$

where w is the frequency, k is Boltzmann's constant, T is the absolute temperature and β the absorption coefficient. This exponential tail would

only be of major significance where infrared transmittance is concerned if it was in close proximity to the wavelengths of interest. The most promising attempt to construct a theoretical basis for this Urbach behaviour is by Dow and Redfield (1972). They found that the exponential absorption edges could be understood as due to electronic field induced ionisation of the exciton. The source of the ionising electric field could be longitudinal optical (LO) phonons, impurities or piezoelectric phonons. The theory was able to give a qualitative prediction of the temperature dependence of optical absorption edge shapes in the alkali halides.
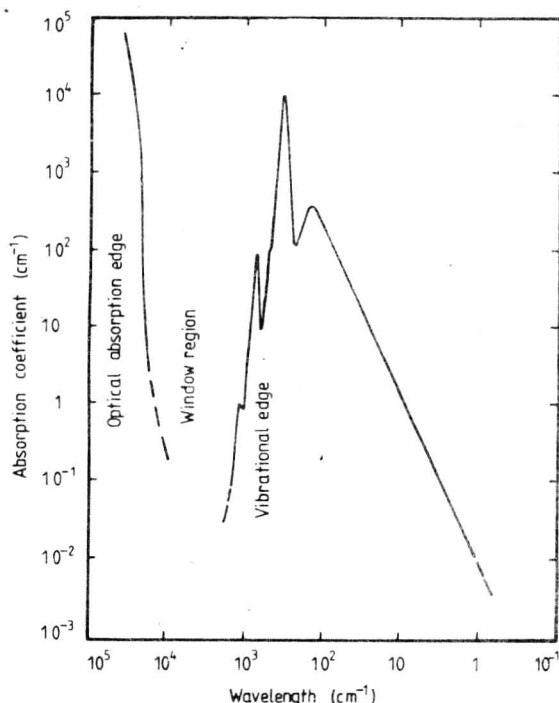
Figure 2.1 The transmittance of As_2S_3 glass showing the UV and vibrational absorption edges and the window region (Strom *et al* 1974).

The long wavelength cut-off in semiconductors and insulators is set by lattice absorptions as illustrated in figure 2.1. These lattice absorptions result from vibrational modes of the atoms in these materials. In ionic crystals vibrations of large amplitude will occur when incident radiation is of the same frequency as the resonant frequency of the atomic units and this is termed the reststrahl frequency. These atomic units must possess a permanent dipole moment which can be activated by the oscillating electric field of the incident radiation. Non-polar solids would be expected to be infrared

inactive but usually exhibit induced dipole effects. For example, a non-ionic solid can have an effective charge and thus a dipole moment if the atoms are not identical. Induced dipole moments are also possible in elemental materials such as diamond and silicon. These homo-polar materials do not possess a permanent dipole moment but an infrared inactive vibrational mode may induce charges on the atoms and a second mode may simultaneously cause a vibration of these charged atoms. These second-order effects are likely to be of low magnitude but nevertheless they are likely to absorb infrared radiation in solids of useful thickness and hence limit the transmittance. The fundamental absorption frequency can be calculated for a linear polar diatomic molecule consisting of two point masses m_1 and m_2. The frequency of vibration, V, of the simple harmonic motion of the two masses along a line joining them is given by (Dekker 1960)

$$V = \frac{1}{2\pi}(K/M)^{1/2} \tag{2.3}$$

where K is the force constant and M is the reduced mass:

$$M = \left(\frac{1}{m_1} + \frac{1}{m_2}\right).$$

If an anharmonic oscillator is considered in the case of a real material then a series of overtone vibrational bands arises in addition to the fundamental frequency. The long wavelength cut-off of a material is usually set by the first overtone of the fundamental lattice absorption.

From equation (2.3) it is clear that the smaller the force constants or the weaker the bonding in a solid, and the larger the atomic masses in a solid, then the lower will be the frequency of the fundamental absorption and hence the long wavelength transmittance limit will be extended further into the infrared. This leads to a problem in that materials exhibiting far and very far infrared transmittance are physically weak because of their weak bonding and tend to possess poor thermal properties. However, there are some exceptions amongst the simpler crystalline structures, specifically the diamond cubic structure found in such materials as silicon and germanium. The strong bonds and light atoms in this structure are able to yield good physical properties as well as very useful transmittance. This is caused by the lack of permanent dipole moments and largely inactive infrared first-order vibrational modes in these simple structures. However, when multi-element materials with non-cubic crystalline or amorphous structures are considered, then these general rules concerning bond strength and atomic masses can be applied in determining the position of the long wavelength cut-off.

Recently several investigations have shown how the infrared absorption decreases as the frequency becomes much greater than the fundamental lattice absorption frequencies and the prominent overtone frequencies in

materials such as the alkali halides (Sparks and Sham 1973), the alkaline earth fluorides (Lipson *et al* 1976), and in semiconductors (Deutch 1975). Highly purified samples of these materials exhibit an absorption coefficient, β, in this multiphonon region which reduces exponentially (Bendow 1975). This exponential tail can be represented by

$$\beta \simeq A e^{-\gamma w} \tag{2.4}$$

where A and γ are material dependent parameters and w is the frequency.

The temperature dependence of equation (2.4) has been shown to vary as some power of the temperature at high temperature and becomes temperature independent at low temperatures (McGill 1975). Detailed discussions of phonons in solids are given by Mitra and Gielisse (1965) and by Wang (1966) and multiphonon processes are discussed by Mitra and Bendow (1975). For present purposes, if the lattice vibrations or phonons in a periodic crystal lattice are treated as harmonic oscillators coupled to their nearest neighbour oscillations, then both transverse and longitudinal modes of oscillation with different velocities transmit the energy across the crystal. Where there is more than one atom per unit cell the adjacent atoms can oscillate in and out of phase with one another and these oscillations are termed acoustic and optical phonons respectively. The phonons can be classified into four groups called longitudinal optical (LO), transverse optical (TO), longitudinal acoustic (LA) and transverse acoustic (TA). Several of these phonons add together to yield an individual Gaussian contribution to the overall absorption tail. It is the summation of all of these individual contributions resulting from each particular crystal structure and unit cell which yields the exponential absorption between the transparent region and the fundamental lattice absorption frequencies.

Thus the fundamental absorption processes which limit the transparency range of insulators and semiconductors are due to electronic transitions across the band gap at short wavelengths or lattice vibrations at longer wavelengths. The absorption coefficient on the long wavelength side of the band gap and on the short wavelength side of the lattice absorption exhibits an exponential dependence on frequency.

Additionally, in semiconductors free electron absorption is important in the region of transparency besides the exponential tails of the absorption edges. The effect of free carriers on the optical properties becomes important at wavelengths larger than the intrinsic electronic absorption edge and involves only the energy band containing the carriers and is described as an intraband effect (Willardson and Beer 1967). There are in addition interband effects which involve another energy band and these transitions give rise to absorption bands at specific wavelengths. The absorption coefficient, β_c, dependent on free carriers can be calculated using

$$\beta_c = \frac{N\lambda^2 e^3}{\mu \pi n m^{*2} c^3} \tag{2.5}$$