Crystal Reference Guide

Thermo Electron Spectroscopy

Thermo Nicolet

Introduction

Thermo Nicolet is proud to present the Crystal Reference Guide. This guide is designed to help FT-IR users determine the crystal materials best-suited for their infrared sampling needs. Thermo Nicolet provides this reference guide and a toll free number to use when in need of assistance. Major considerations in choosing materials are frequency range, solubility of the sample, refractive index, reactivity with the sample, and mechanical and thermal characteristics.*

Thermo Nicolet offers an unprecedented choice of infrared transmission windows in all shapes, sizes and materials. The windows fit in all of Thermo Nicolet standard cells and those made by other manufacturers. Thermo Nicolet cuts, drills and polishes windows to exacting tolerances. At each step of fabrication, rigid quality controls ensure uniformity and excellence.

Our purpose is to make your job easier by providing the right technology for analyzing samples accurately, easily and cost effectively.

Our Products...Innovative, Reliable and Easy to Use!

If you desire additional information, please contact Thermo Nicolet at 800-THE-FTIR or 203-926-8998.

** The information in this booklet has been verified to be accurate, however, Thermo Nicolet cannot be held responsible for any errors or omissions.*

How to Select an Infrared Transmission Window

Currently, there are over a dozen different infrared window materials to choose from, each with its own characteristic properties. There are several factors that must be considered when choosing the optimum window material for your application needs. These include:

- the spectral range to be studied
- the chemical properties of the sample versus that of the window
- the physical properties of the window
- the relative cost for the specific need

Transmission Range

The factors affecting the amount of energy through the transmission cell (exclusive of the sample) are:

- the transmission range of the window
- the effective thickness of the window
- the amount of energy lost due to reflection at the window surfaces
- the potential energy losses due to usage, such as marring and fogging

The useful transmission ranges that are listed in this publication were established at the point where the transmission level is reduced to less than 50% of the maximum energy for a single window, thus thinner windows of the same material will transmit to lower wavenumber (longer wavelength).

When using windows with a high refractive index, there is significant energy loss due to reflection off the window surfaces and there may be strong sinusoidal waves called interference fringes. These interference fringes are caused by the reflection of infrared radiation within a cell whose windows have parallel faces and are perpendicular to the incident radiation. The intensity of the fringes varies with the refractive index of the material, the greater the refractive index the stronger the fringes. The air gap between the windows of a cell defines the period of the fringes, a small gap (a 0.015 mm pathlength cell) gives a high period of fringes, a large gap (0.50 mm pathlength cell) gives a low period of fringes. The fringe pattern is very useful in calculating the absolute pathlength of the cell (see *How to Calibrate Infrared Absorption Cells* on page 3).

Chemical Properties

An important factor to consider when choosing the appropriate window materials for a specific application are the chemical properties of both the sample and the window material. Samples that react with a window material will erode the inner surfaces of the cell. The relative water solubility, and the common samples or solvents that will erode the window surfaces are often listed in property charts. Solubility data are given in terms of the number of grams of the material that under equilibrium conditions will dissolve in 100 milliliters of water at room temperature. The solubility in water should not be confused with the degree to which a window material is hygroscopic. A material that is hygroscopic readily absorbs water from the atmosphere and will cause the window to fog or become opaque, reducing the ability to transmit energy.

Physical Properties

An ideal window material must also be compatible with the physical properties of the sample; such as hardness. With a very hard sample, soft window materials should not be used. To a large extent, the measures of hardness are empirical and comparative. Most methods of measuring hardness are based on pressing a material with a specified force with an indentor of a prescribed shape. The shape determines whether the method is called Brinell, Vickers or Knoop. Hardness measurements can vary with applied load, duration of the load and speed of application and release. The variability depends on material properties of creep, cold flow and stress relief by minute cracks. Some of the softer materials, such as potassium bromide and sodium chloride can be repolished by hand when they become etched or scratched. The very hard materials, such as silicon and sapphire resist scratching, but are extremely difficult to repolish by hand.

Cost vs. Need

Two basic types of transmission cells can be selected; sealed cells with the appropriate holder, or demountable cells with the appropriate holder. A sealed cell has precision aligned windows and provides leakproof operation. It consists of one drilled window and one undrilled window sealed together. The windows are separated by a metal spacer that determines the pathlength, and are amalgam sealed together. Sealed cells have a shelf life of approximately 12 months due to the amalgam seal. The windows are perfectly parallel and the pathlength is known, therefore the cell can easily be calibrated for quantitative measurements and other precision spectroscopic analyses. Sealed cells can be used with highly volatile samples, such as ethyl ether, without the risk of leakage.

Demountable cells are a practical and economical alternative to sealed cells. Demountable refers to the ability to easily change the pathlength of the cell. These cells are composed of one drilled window, one undrilled window of the same size and material, a spacer (which is typically Teflon®) and a gasket. These cells are invaluable when used with viscous, or hard to clean samples, because they can be easily disassembled, cleaned and reassembled. A demountable cell should be used when the correct pathlength for a specific application must be determined through experimental research. The pathlength of demountable cells can be altered by changing the spacer thickness.

How to Calibrate Infrared Absorption Cells

One of the easiest ways to calculate the pathlength of a cell is by the interference fringe method. This can be done in any spectrometer. The interference fringe is caused by two parallel smooth surfaces in close proximity (less than 1 mm) to each other.

Fringe Method

1. Collect a background file with the sample compartment empty.
2. Place the empty cell in the FT-IR spectrometer on the usual sample slide.
3. Collect a sample file.
4. Display spectra in %Transmittance
5. Calculate the cell thickness using one of the following equations:

To Calculate Using Wavenumbers:

$$L\ (mm) = \frac{n\ (10)}{2\ (W_1 - W_2)}$$

where L = cell thickness (mm)

W_1 = starting wavenumber (cm^{-1})

W_2 = ending wavenumber (cm^{-1})

n = number of fringes between W_1 and W_2

To Calculate Using µm (Microns):

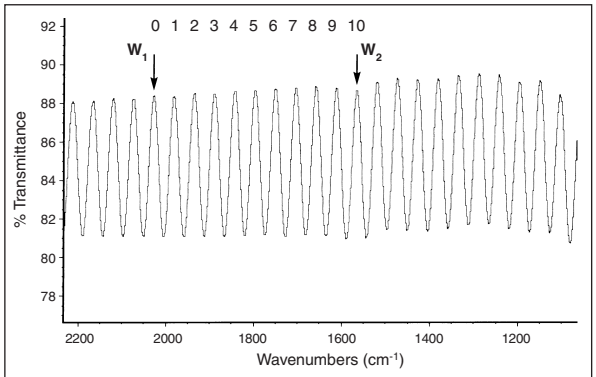
$$L\ (mm) = \frac{n\ W_1 W_2}{2\ (W_2 - W_1)\ (1000)}$$

where L = cell thickness (mm)

W_1 = starting wavelength (µm)

W_2 = ending wavelength (µm)

n = number of fringes between W_1 and W_2



Sample Calculation:

Data from the spectrum above

$n = 10$, $W_1 = 2040$ $W_2 = 1570$

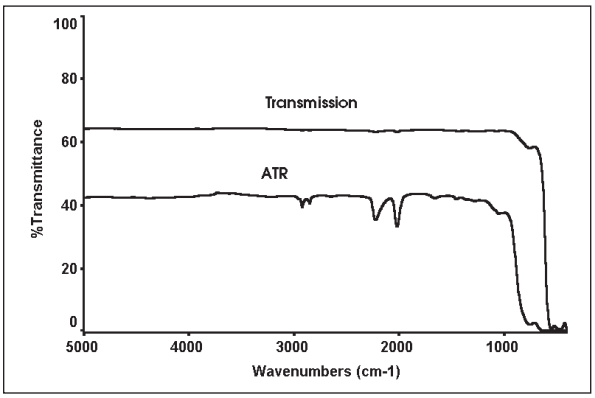
Using the formula, calculate using wavenumbers, the thickness can be calculated by substituting the numbers.

$$L = \frac{n\ (10)}{2(W_1 - W_2)} = \frac{10\ (10)}{2\ (2040 - 1570)} = \frac{100}{2\ (470)}$$

L = 0.106 mm = 106 microns

AMTIR (GeAsSe Glass)

AMTIR[-1] (Amorphous Material Transmitting Infrared Radiation or GeAsSe Glass) is insoluble in water and very resistant to corrosion in acidic solutions. In case of long term exposure (one week), it will dissolve in alkaline solutions. It can be used to 300°C. AMTIR is a good ATR material due to its refractive index and spectral range.

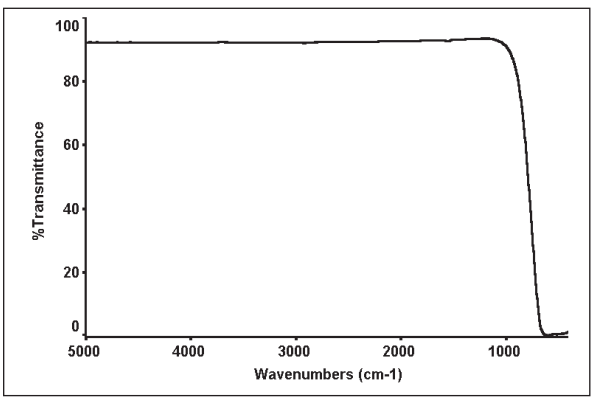


SPECIFICATIONS

Transmission Range: 11,000-625 cm^{-1}
ATR Spectral Range (12 reflection crystal)**:** 11,000-840 cm^{-1}
Refractive Index: 2.5
% Transmittance (thickness): 68% @ 2-mm thickness
Cleaning Agents: Alcohol, Acetone, H_2O
Solubility In Water (100g H_2O @25°C)**:** insoluble
Density g/cm³: 4.4
Solvents Which Attack: Alkalies
Max Temp In Air °C: 300
Melting Point °C: 370
Hardness kg/mm² (Knoop #)**:** 170
pH Range: 1-9
Depth of Penetration*: 1.70

Barium Fluoride (BaF_2)

BaF_2 has greater transmission range than CaF_2. BaF_2 must be handled with care because it is easily cleaved by thermal or mechanical shock. The useful temperature range is narrower than for CaF_2 because BaF_2 reacts with air at 500°C and can be used only to 800°C in a dry atmosphere. It should not be used with solutions of ammonium salts. Commonly used for infrared transmission windows.

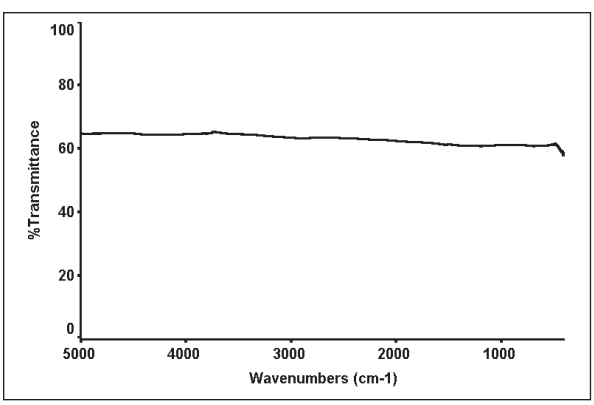


SPECIFICATIONS

Transmission Range: 50,000-740 cm^{-1}
Refractive Index: 1.42
% Transmittance (thickness)**:** 90% @ 3-mm thickness
Cleaning Agents: Acetone, alcohol
Solubility In Water (100g H_2O @25°C)**:** 0.17 grams
Density g/cm³: 4.83
Solvents Which Attack: NH_4+ salts, acids
Max Temp In Air °C: 500
Melting Point °C: 1,280
Hardness kg/mm² (Knoop #)**:** 82
Composition: Single crystal
Crystal Class: Cubic
pH Range: 5-8

Cadmium Telluride (CdTe)

CdTe is attacked by oxidizers and is slightly soluble in acids. CdTe is softer than ZnS and ZnSe. Useful for infrared transmission windows.



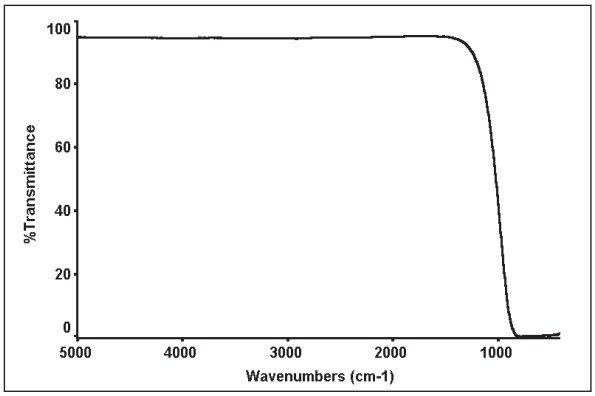
SPECIFICATIONS

Transmission Range: 20,000-360 cm^{-1}
Refractive Index: 2.67
% Transmittance (thickness)**:** 40% @ 5-mm thickness
Cleaning Agents: Alcohol, acetone
Solubility In Water (100g H_2O @25°C)**:** Insoluble
Density g/cm³: 6.2
Solvents Which Attack: Acids, HNO_3
Max Temp In Air °C: 300
Melting Point °C: 1,040
Hardness kg/mm² (Knoop #): 56
Composition: Single crystal
Crystal Class: Cubic
pH Range: 1-9
Depth of Penetration*: 1.39

** Assumes a 45 degree crystal and 1,000 cm^{-1} with a sample refractive index of 1.5*

Calcium Fluoride (CaF_2)

One of the hardest crystal materials, CaF_2 is particularly useful in high pressure cells. It resists most acids and alkalides. It is non-hygroscopic at room temperature but will react with air at elevated temperatures. If kept dry, crystal can be used to 900°C. CaF_2 should not be used with solutions of ammonium salts. Commonly used for infrared transmission windows.

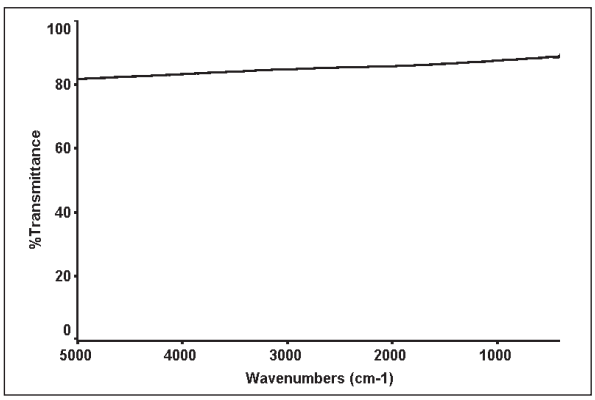


SPECIFICATIONS

Transmission Range: 50,000-1,111 cm^{-1}
Refractive Index: 1.39
% Transmittance (thickness)**:** 90% @ 4-mm thickness
Cleaning Agents: Acetone, alcohol
Solubility In Water (100g H_2O @25°C): 0.0013 grams
Density g/cm³: 3.18
Solvents Which Attack: NH_4+ salts, acids
Max Temp In Air °C: 900
Melting Point °C: 1,360
Hardness kg/mm² (Knoop #)**:** 158
Composition: Single crystal
Crystal Class: Cubic, cleaves on (111) plane
pH Range: 1-9

Cesium Iodide (CsI)

CsI is very useful because of its extended transmission range and good shock resistance. However, it is very hygroscopic and easily scratched. It reacts with more organic compounds than NaCl or KBr. This window material is considered for its extended low-end spectral range, but due to its soft and hygroscopic nature, it is not a useful material for windows. We recommend diamond windows for extended, far-IR operation.

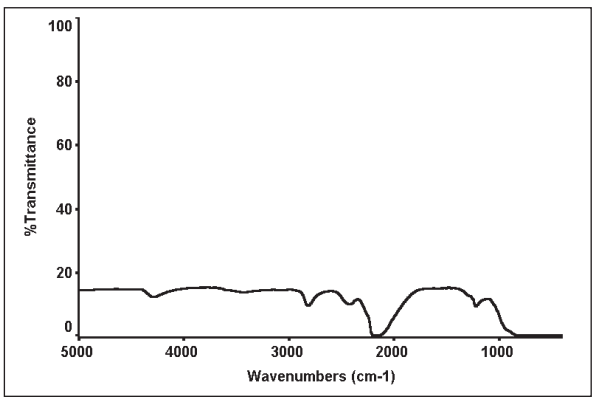


SPECIFICATIONS

Transmission Range: 40,000-200 cm^{-1}
Refractive Index: 1.74
% Transmittance (thickness)**:** 92% @ 2-mm thickness
Cleaning Agents: Anhydrous solvents
Solubility In Water (100g H_2O @25°C)**:** 44.4 grams
Density g/cm³: 4.5
Solvents Which Attack: Lower alcohols, wet solvents
Max Temp In Air °C: 200
Melting Point °C: 621
Hardness kg/mm² (Knoop #)**:** 20
Composition: Single crystal
Crystal Class: Cubic
pH Range: N/A (due to water solubility)

Chalcogenide (AsSeTe Glass)

Chalcogenide is the best material for mid-Infrared Fiber Optics. The Chalcogenide fiber is composed of AsSeTe glass, is chemically inert and mid-infrared transmissive.



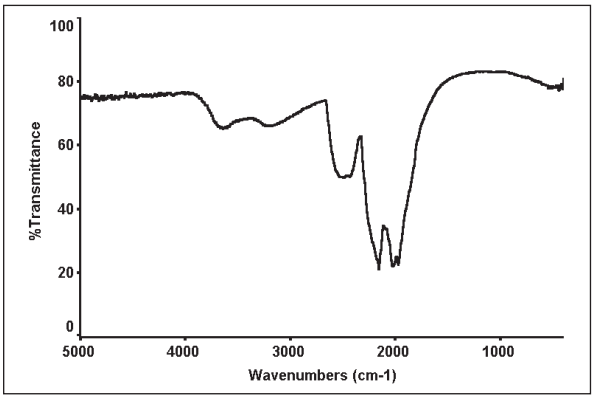
SPECIFICATIONS

Transmission Range: 4,000-900 cm^{-1}
Refractive Index: 2.8
% Transmittance (thickness)**:** 15% @ 1.5 m cable
Cleaning Agents: Water, acetone, CH_2Cl_2
Solubility In Water (100g H_2O @25°C)**:** Insoluble
Density g/cm³: 4.4
Solvents Which Attack: Strong acids, bases
Max Temp In Air °C: 100
Melting Point °C: 170
Hardness kg/mm² (Knoop #)**:** NA
Composition: Single Crystal
Crystal Class: Cubic
pH Range: 1-9
Depth of Penetration*: 1.23

** Assumes a 45 degree crystal and 1,000 cm^{-1} with a sample refractive index of 1.5*

Diamond

The Type IIa diamond has a transparency in the IR from 4,000 to 33 cm^{-1} with spectral bands between 2,600 and 1,600 cm^{-1} with the fingerprint region clear. These bands ratio easily, leaving the sample spectrum unaffected. The diamond is especially useful for high-pressure cells and ATR crystals due to its refractive index and chemical resistance to attack.

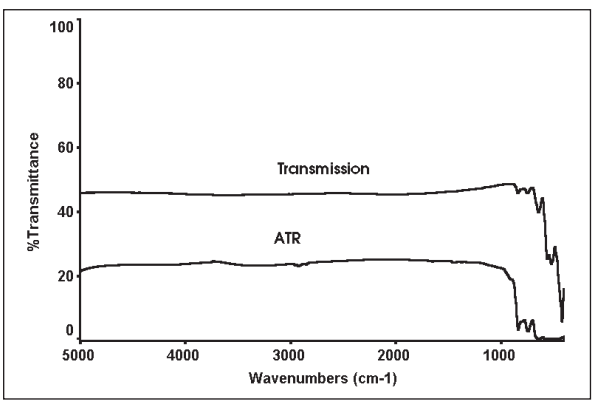


SPECIFICATIONS

Transmission Range: 4,500-2,500 cm^{-1} & 1,667-33 cm^{-1}
Refractive Index: 2.4
% Transmittance (thickness)**:** 70% @ 1-mm thickness
Cleaning Agents: Alcohol, acetone, H_2O
Solubility In Water (100g H_2O @25°C)**:** Insoluble
Density g/cm³: 3.51
Solvents Which Attack: $K_2Cr_2O_7$, conc H_2SO_4
Max Temp In Air °C: 750
Melting Point °C: 3,500
Hardness kg/mm² (Knoop #)**:** 7,000
Composition: Crystalline carbon, Single crystal
Crystal Class: Cubic
pH Range: 1-14
Depth of Penetration*: 2.01

Germanium (Ge)

Ge is a hard, brittle substance. It has low transmission levels due to high reflection losses. Ge is soluble in hot sulfuric acid and aqua regia, but insoluble in water. A high refractive index makes Ge an excellent choice for ATR analysis of carbon-filled materials.

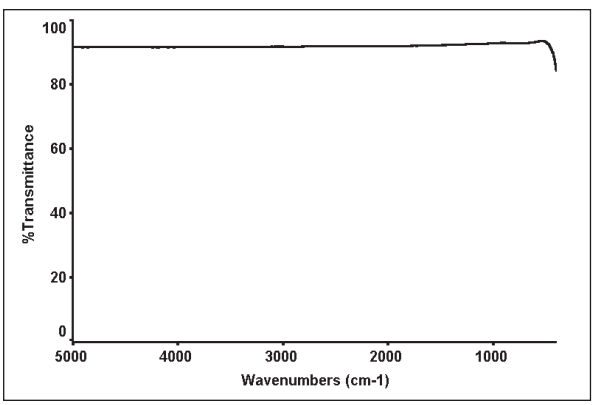


SPECIFICATIONS

Transmission Range: 5,500-475 cm^{-1}
ATR Spectral Range: 5,500-675 cm^{-1}
Refractive Index: 4.0
% Transmittance (thickness)**:** 50% @ 2-mm thickness
Cleaning Agents: Alcohol, acetone, H_2O
Solubility In Water (100g H_2O @25°C)**:** Insoluble
Density g/cm³: 5.32
Solvents Which Attack: Hot H_2SO_4, aqua regia
Max Temp In Air °C: 125
Melting Point °C: 936
Hardness kg/mm² (Knoop #)**:** 550
Composition: Single crystal
Crystal Class: Cubic
pH Range: 1-14
Depth of Penetration*: 0.66

Potassium Bromide (KBr)

The most common window material because it covers a wider spectral range than NaCl. KBr offers good resistance to thermal and mechanical shock. KBr windows are easy to polish but are more hygroscopic than NaCl. Commonly used for infrared transmission windows.



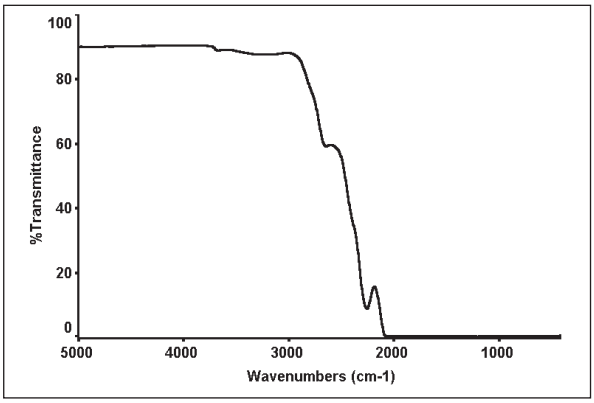
SPECIFICATIONS

Transmission Range: 40,000-400 cm^{-1}
Refractive Index: 1.52
% Transmittance (thickness)**:** 90.5% 4.0-mm thickness
Cleaning Agents: Anhydrous alcohols
Solubility In Water (100g H_2O @25°C)**:** 53.5 grams
Density g/cm³: 2.75
Solvents Which Attack: Lower alcohols, wet solvents
Max Temp In Air °C: 300
Melting Point °C: 730
Hardness kg/mm² (Knoop #)**:** 7
Composition: Single crystal
Crystal Class: Cubic, cleaves on (100) planes
pH Range: N/A (due to water solubility)

** Assumes a 45 degree crystal and 1,000 cm^{-1} with a sample refractive index of 1.5*

Quartz (SiO_2)

Quartz is used in the ultraviolet-visible and near infrared spectral regions. Infrared Quartz is of high purity with minimal OH content. Quartz is water insoluble.

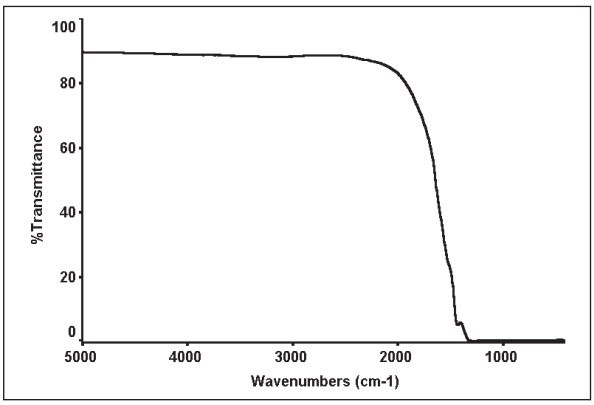


SPECIFICATIONS

Transmission Range: 25,000-2,200 cm^{-1}
Refractive Index: 1.4
% Transmittance (thickness)**:** 90% @ 3-mm thickness
Cleaning Agents: Alcohol, acetone, H_2O
Solubility In Water (100g H_2O @25°C)**:** Insoluble
Density g/cm³: 2.65
Solvents Which Attack: HF, some hot acids and bases
Max Temp In Air °C: 1,100
Melting Point °C: 1,470
Hardness kg/mm² (Knoop #)**:** 174
Composition: Natural crystal
Crystal Class: Hexagonal (birefringent)
pH Range: 1-14

Sapphire (Al_2O_3)

Sapphire, a single crystal aluminum oxide, is a very hard material, chemically inert and is birefringent. It is attacked by concentrated acids and bases.

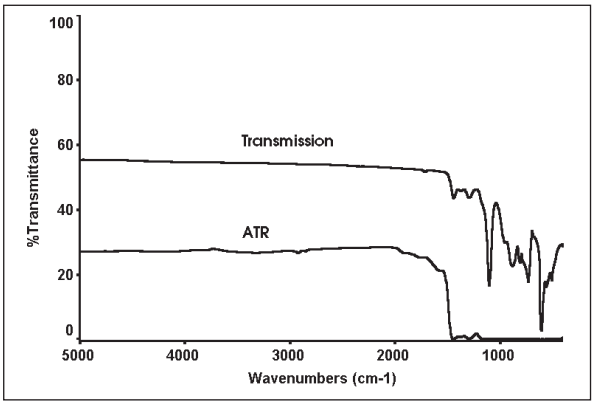


SPECIFICATIONS

Transmission Range: 50,000-1,525 cm^{-1}
Refractive Index: 1.5
% Transmittance (thickness)**:** 70% @ 1-mm thickness
Cleaning Agents: Alcohol, acetone, H_2O
Solubility In Water (100g H_2O @25°C)**:** Insoluble
Density g/cm³: 4.0
Solvents Which Attack: Slightly in acids and alkalis
Max Temp In Air °C: 1,700
Melting Point °C: 2,030
Hardness kg/mm² (Knoop #)**:** 1,370
Composition: Single crystal
Crystal Class: Hexagonal
pH Range: 1-14

Silicon (Si)

Optical grade Si is very similar to Ge, but has better resistance to mechanical and thermal shock. Si is soluble in a hydrofluoric and nitric acids mixture. As an ATR material, its moderate refractive index limits its depth of penetration in highly absorbing materials. As an infrared transmission window, it provides excellent performance above 1,600 cm^{-1}.



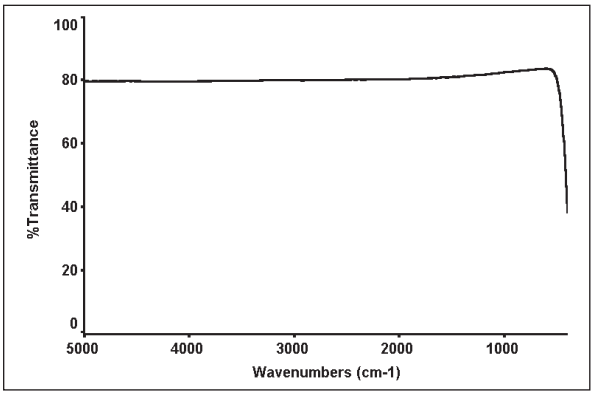
SPECIFICATIONS

Transmission Range: 8,300-660 cm^{-1} & 360-70 cm^{-1}
ATR Spectral Range: 8,300-1,500 cm^{-1} & 360-120 cm^{-1}
Refractive Index: 3.4
% Transmittance (thickness)**:** 55% @ 2.5-mm thickness
Cleaning Agents: Alcohol, acetone, H_2O
Solubility In Water (100g H_2O @25°C)**:** Insoluble
Density g/cm³: 2.33
Solvents Which Attack: HF & HNO_3
Max Temp In Air °C: 300
Melting Point °C: 1,420
Hardness kg/mm² (Knoop #)**:** 1,150
Composition: Polymorphic
Crystal Class: Cubic
pH Range: 1-12
Depth of Penetration*: 0.84

** Assumes a 45 degree crystal and 1,000 cm^{-1} with a sample refractive index of 1.5*

Silver Chloride (AgCl)

Silver Chloride is a soft, non-hygroscopic material, but it will darken with prolonged exposure to UV light. Prolonged contact with base metals where moisture is present will cause corrosion.



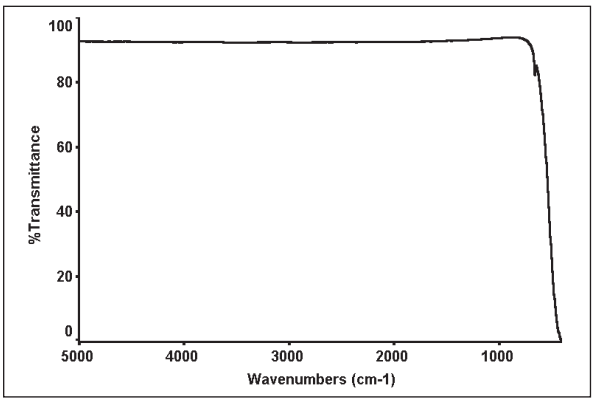
AgCl is malleable and will cold flow under pressure. It is insensitive to thermal and mechanical shock. Commonly used for infrared transmission windows.

SPECIFICATIONS

Transmission Range: 25,000-360 cm^{-1}
Refractive Index: 1.98
% Transmittance (thickness)**:** 84% @ 3-mm thickness
Cleaning Agents: Acetone CH_2Cl_2
Solubility In Water (100g H_2O @25°C)**:** .00015 grams
Density g/cm³: 6.47
Solvents Which Attack: Complexing Agents, NH_4OH
Max Temp in Air °C: 200
Melting Point °C: 457.7
Hardness kg/mm² (Knoop #)**:** 9.5
Composition: Single Crystal
Crystal Class: Cubic, does not cleave
pH Range: N/A (due to water solubility)

Sodium Chloride (NaCl)

One of the most useful materials because of its useful spectral range and low cost. NaCl withstands thermal and mechanical stress fairly well and is easily polished. NaCl is soluble in water. Commonly used for infrared transmission windows.

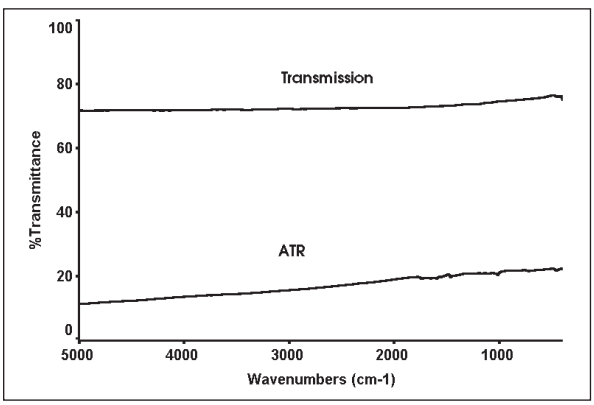


SPECIFICATIONS

Transmission Range: 40,000-625 cm^{-1}
Refractive Index: 1.49
% Transmittance (thickness)**:** 91.5% @ 4-mm thickness
Cleaning Agents: Anhydrous solvents
Solubility In Water (100g H_2O @25°C)**:** 35.7 grams
Density g/cm³: 2.17
Solvents Which Attack: Lower alcohols, wet solvents
Max Temp In Air °C: 400
Melting Point °C: 801
Hardness kg/mm² (Knoop #)**:** 15
Composition: Single crystal
Crystal Class: Simple cubic, cleaves on (100) planes
pH Range: N/A (due to water solubility)

Thallium Bromide-Iodide (KRS-5)

KRS-5 is used as a transmission window and as ATR crystals because it has a wide spectral range, high-refractive index and does not easily fracture. It is slightly soluble in water, soluble in bases and insoluble in acids. This material should not be used with solutions of ammonium salts. KRS-5 is toxic, but only if the dust is ingested or absorbed into a cut. Although it is used as an ATR material, it has been replaced by ZnSe, due to toxicity concerns.



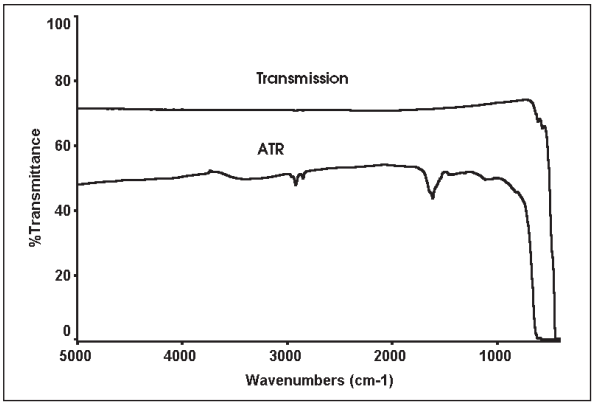
SPECIFICATIONS

Transmission Range: 20,000-250 cm^{-1}
ATR Spectral Range: 20,000-400 cm^{-1}
Refractive Index: 2.37
% Transmittance (thickness)**:** 70% @ 2-mm thickness
Cleaning Agents: MEK
Solubility In Water (100g H_2O @25°C)**:** 0.05 grams
Density g/cm³: 7.37
Solvents Which Attack: Complexing agents
Max Temp In Air °C: 200
Melting Point °C: 414.5
Hardness kg/mm² (Knoop #)**:** 40
Composition: Mixed crystal
Crystal Class: Cubic, Does not cleave
pH Range: 5-8
Depth of Penetration*: 2.13

** Assumes a 45 degree crystal and 1,000 cm^{-1} with a sample refractive index of 1.5*

Zinc Selenide (ZnSe)

Zinc Selenide (ZnSe) is a good window material because it is insoluble in water and very resistant to most solvents which attack. It is only slightly soluble in acids. Because of its low-reflection losses in the infrared, it is a good material for ATR and Cylindrical Internal Reflection (CIR) crystals.

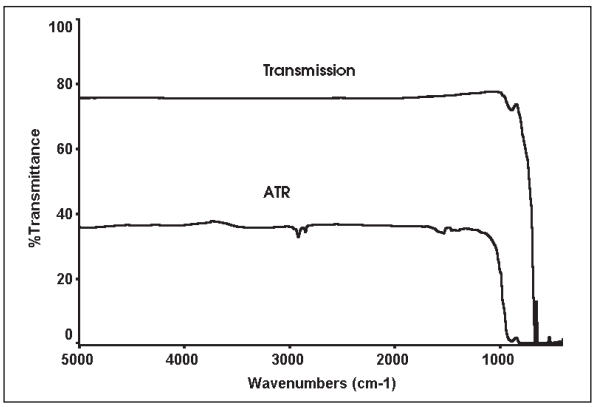


SPECIFICATIONS

Transmission Range: 20,000-454 cm^{-1}
ATR Spectral Range: 20,000-650 cm^{-1}
Refractive Index: 2.4
% Transmittance (thickness)**:** 65 (1.0 mm)
% Transmittance (ATR min.)**:** 15 +
Cleaning Agents: Alcohol, acetone, H_2O
Solubility In Water (100g H_2O @25°C)**:** Insoluble
Density g/cm³: 5.27
Solvents Which Attack: Acids, strong alkalies
Max Temp In Air °C: 300
Melting Point °C: 1,520
Hardness kg/mm² (Knoop #)**:** 137
Composition: Polycrystalline
Crystal Class: Cubic
pH Range: 5-9
Depth of Penetration*: 2.01

Zinc Sulfide (ZnS)

Zinc Sulfide is insoluble in water but can be attacked by strong oxidizing agents. It offers good resistance to thermal and mechanical shock.



SPECIFICATIONS

Transmission Range: 17,000-720 cm^{-1}
ATR Spectral Range: 17,000-950 cm^{-1}
Refractive Index: 2.2
% Transmittance (thickness)**:** 70 (1.0 mm)
Cleaning Agents: Alcohol, acetone
Solubility In Water (100g H_2O @25°C)**:** 0.00069 grams
Density g/cm³: 4.08
Solvents Which Attack: Acids
Max Temp In Air °C: 300
Melting Point °C: 1,830
Hardness kg/mm² (Knoop #)**:** 178
Composition: Polycrystalline
Crystal Class: Cubic
pH Range: 5-12
Depth of Penetration*: 3.86

** Assumes a 45 degree crystal and 1,000 cm^{-1} with a sample refractive index of 1.5*

Thermo Electron Spectroscopy
5225 Verona Road • Madison, WI 53711-4495 • U.S.A.
TEL: 800-201-8132, 608-276-6100 • FAX: 608-273-5046
E-MAIL: nicinfo@thermonicolet.com
WEB: www.thermo.com/thermonicolet

P/N 169-722300 5/02

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