

CVD ZINC SULFIDE™

Application

Chemically vapor deposited zinc sulfide (CVD ZnS) is the low cost alternative for infrared windows, domes and optical elements. With a fracture strength double that of zinc selenide and high hardness, zinc sulfide has been used successfully in many military applications requiring mechanical resistance to hostile environments. Missile domes and external windows for military aircraft have been produced by Advanced Materials' CVD ZINC SULFIDE as the mechanical features of this material allow for high resistance to rain and dust. Its low cost also makes it attractive for commercial applications.

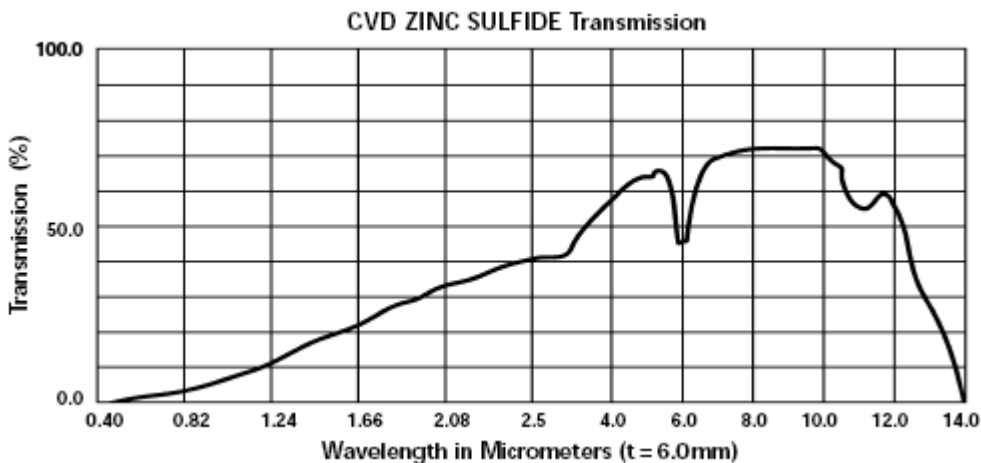
Advanced Materials' CVD ZINC SULFIDE is chemically inert, non-hygroscopic, highly pure, theoretically dense, and easily machined. Like zinc selenide, zinc sulfide displays a high level of index of refraction homogeneity and offers imaging uniformity across the 8-12 micron waveband. This material also transmits in the mid-wave IR region, but with higher absorption and scatter as the wavenumber increases.

Custom diameters, rectangles, CNC-profiled blanks, generated lens blanks, prisms, and near-net shape domes can be made to your specifications. Sheet material is also available.

Advanced Materials' CVD ZINC SULFIDE is also available as an evaporative source material. It is supplied in specified lump sizes (2-20 mm), which to minimize surface contamination, are hand selected to be free from saw cut, abraded or polished edges.

Optical Properties

10% transmission limits (t=6 mm)	1.0 - 14 μm
Index of refraction inhomogeneity ($\Delta n/n$) (ppm @ 10.6 μm)	<100
Thermo-optic coefficient, dn/dT (298-358K) (avg. values, see back page for more details)	
(K^{-1} @ 1.15 μm)	4.6×10^{-5}
(K^{-1} @ 3.39 μm)	4.3×10^{-5}
(K^{-1} @ 10.6 μm)	4.1×10^{-5}
Bulk absorption coefficient (cm^{-1} @ 10.6 μm)	2.0×10^{-1}



Physical Properties

These properties are typical but do not constitute specifications.

Crystal structure		cubic
Grain size	(diameter)	2 - 8 μm
Density	(g cm^{-3} @ 298 K)	4.09
Resistivity	(Ωcm)	$\approx 10^{12}$
Chemical purity	(%)	99.996

For dielectric constant data, please request the Dielectric Properties bulletin.

Thermal Properties

Coefficient of Thermal Expansion		
	(K^{-1} @ 273 K)	6.6×10^{-6}
	(K^{-1} @ 373 K)	7.3×10^{-6}
	(K^{-1} @ 473 K)	7.7×10^{-6}
Thermal conductivity		
	($\text{JK}^{-1}\text{m}^{-1}\text{s}^{-1}$ @ 298 K)	16.7
Heat capacity	($\text{Jg}^{-1}\text{K}^{-1}$ @ 298 K)	0.469

Maximum operating temperature will depend on the environment.

**Indices of Refraction (n) of
CVD ZINC SULFIDE¹
as a function of wavelength at room temperature (20°C)**

Wavelength (μm)	n	Wavelength (μm)	n
0.42	2.516	7.00	2.232
0.46	2.458	7.40	2.228
0.50	2.419	7.80	2.225
0.54	2.391	8.20	2.221
0.58	2.371	8.60	2.217
0.62	2.355	9.00	2.212
0.66	2.342	9.40	2.208
0.70	2.332	9.80	2.203
0.74	2.323	10.20	2.198
0.78	2.316	10.60	2.192
0.82	2.310	11.00	2.186
0.86	2.305	11.40	2.180
0.90	2.301	11.80	2.173
0.94	2.297	12.20	2.167
0.98	2.294	12.60	2.159
1.00	2.292	13.00	2.152
1.40	2.275	13.40	2.143
1.80	2.267	13.80	2.135
2.20	2.263	14.20	2.126
2.60	2.260	14.60	2.116
3.00	2.257	15.00	2.106
3.40	2.255	15.40	2.095
3.80	2.253	15.80	2.084
4.20	2.251	16.20	2.072
4.60	2.248	16.60	2.059
5.00	2.246	17.00	2.045
5.40	2.244	17.40	2.030
5.80	2.241	17.80	2.015
6.20	2.238	18.20	1.998
6.60	2.235		

**Thermo-optic Coefficient,
CVD ZINC SULFIDE¹
dn/dT (10⁻⁵K⁻¹)
Wavelength (μm)**

Temp °C	1.15	3.39	10.6
-180	3.5	2.8	2.7
-160	3.7	3.1	3.0
-140	3.8	3.3	3.3
-120	4.0	3.5	3.5
-100	4.1	3.7	3.7
-80	4.2	3.9	3.8
-60	4.3	4.0	3.9
-40	4.4	4.1	4.0
-20	4.5	4.1	4.0
0	4.5	4.2	4.1
20	4.6	4.2	4.1
40	4.6	4.3	4.1
60	4.7	4.3	4.1
80	4.7	4.3	4.1
100	4.7	4.3	4.2
120	4.8	4.4	4.2
140	4.8	4.4	4.3
160	4.9	4.4	4.4
180	4.9	4.5	4.5
200	5.0	4.6	4.7
σ ^a	0.2	0.2	0.2

^aStandard deviation from a third degree polynomial fit.

¹A. Feldman et al, Final Technical Report Feb. 1, 1978 - Sept 30, 1978, National Bureau of Standards Technical Note 933, 53-54

Mechanical Properties

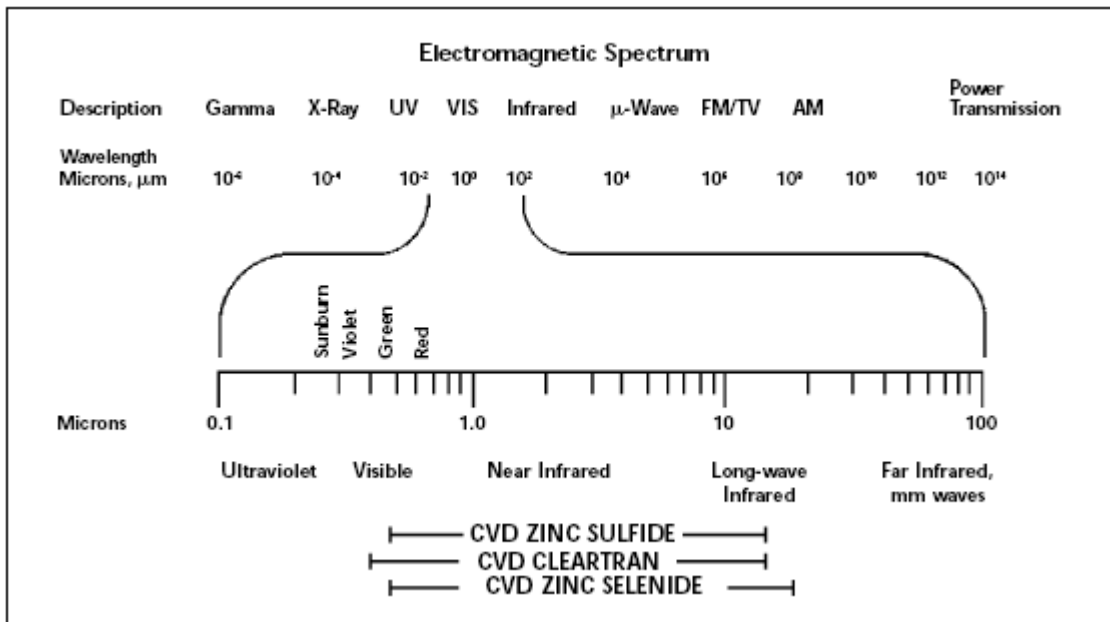
Hardness	Knoop, 50 gm load (kg mm ⁻²)	200 - 235
	Vickers, 1 kg load (kg mm ⁻²)	230
Flexural Strength (modulus of rupture)		
	4 pt. loading (psi)	15 x 10 ³
	4 pt. loading (MPa)	103
	Disc Bursting (MPa)	84
Fracture Toughness (critical stress intensity factor, K _{IC} values)		
	(MPa√m, Vickers, 1 Kg)	0.8
Young's Modulus (elastic modulus)		
	(psi)	10.8 x 10 ⁶
	(GPa)	74.5
Poisson's Ratio		0.29
Rain erosion resistance will depend on the environment.		

Transmission, Attenuation, and Absorption of Infrared Materials

The discussion below is a simplified introduction to the complex subject of determining the transmission, attenuation, and absorption coefficients of Advanced Materials' infrared materials. For a more detailed discussion, please refer to the many textbooks on optical materials.

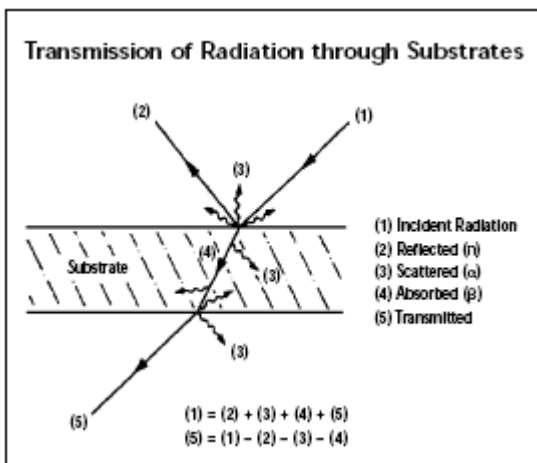
Transmission

CVD ZINC SELENIDE™, CVD ZINC SULFIDE™, CLEARTRAN™, and TUFTRAN™ materials transmit energy in the visible and infrared regions of the electromagnetic spectrum.



All objects emit infrared radiation at temperatures above absolute zero. This radiation travels through the atmosphere as a waveform and is bent or refracted through transmitting media such as Advanced Materials' infrared materials. Infrared radiation follows many of the same physical laws that govern visible light and is referred to as light, radiation, or energy.

Infrared external transmittance can be defined as the ratio of energy which emerges from the final surface of an optical material to the energy which first strikes the optical material. The percent transmittance in a plane parallel plate of an optical material would include the original energy less the amount reflected, scattered, and absorbed. The simplified diagram below shows the effect of reflection, absorption, and scatter on the original energy and resultant transmission.



To determine the theoretical transmission through an uncoated optical material, an optical designer needs to know the material's index of refraction. The index of refraction, n , is simply defined as the ratio of the velocity of light in the material to its velocity in a vacuum ($n=1$). The index is most often measured using a refractometer which measures the angle of refraction at a given wavelength. From the angle of refraction the index can then be computed. For CVD ZINC SELENIDE, CVD ZINC SULFIDE, and CLEARTRAN materials, the indices of refraction are available from Advanced Materials.

When light originating in air ($n \sim 1$) is incident on the surface of an optically transparent material, some of the light is reflected from the surface and some is transmitted into the material. The fraction of light reflected is given by:

Eq. (1)

$$R = \frac{[\cos \theta - \sqrt{n^2 - \sin^2 \theta}]^2}{[\cos \theta + \sqrt{n^2 - \sin^2 \theta}]^2}$$

where θ is the angle of incidence (measured from the normal to the surface) and n is the refractive index of the material. For normal incidence, i.e., $\cos \theta = 1$ and $\sin \theta = 0$, Eq. (1) reduces to:

Eq. (2)

$$R = \frac{(1 - n)^2}{(1 + n)^2}$$

This will determine reflection from the first (front) surface only. Before the ray of light can exit from the opposite side, it undergoes a second reflection from the inside of the second surface. This second reflection also bounces around and if all of this is added up, the total theoretical external transmittance of a polished, uncoated, plane parallel plate, taking into account multiple internal reflections, and assuming there is no absorption or scattering within the material, is:

Eq. (3)

$$T_{\max} = \frac{2n}{(n^2 + 1)}$$

where T_{\max} is the total theoretical external transmittance, which is the maximum transmission possible for an uncoated window. T_{\max} is a function of wavelength since n varies with the wavelength of light.

Attenuation Coefficient

The attenuation coefficient, α , is a measure of the loss in transmission due to absorption and scattering of light in the optical material. The measured transmission T , through an optical window of thickness t , is given by:

Eq. (4)

$$T = \frac{(1 - R)^2 e^{-\alpha t}}{1 - R^2 e^{-2\alpha t}}$$

where R is defined in Eq. (2) and α is the attenuation coefficient which has units of reciprocal length, i.e., cm^{-1} . A less precise, but more commonly used formula is:

Eq. (5)

$$T = (1 - R)^2 e^{-\alpha t}$$

For example, if $\alpha = 0.1 \text{ cm}^{-1}$, $t = 1 \text{ cm}$ and $R = 0.15$, then $T = 0.66$ using Eq. (4) and $T = 0.65$ using Eq. (5). Since most commercially available conventional IR spectrophotometers have an accuracy of $\pm 1\%$ for transmission measurements, in most cases Eq. (5) would be adequate to calculate attenuation coefficients from transmission data provided $T < T_{\max}$. When $T \approx T_{\max}$ Fourier Transform IR (FTIR) spectrometers can be used to determine α . FTIR spectrometers typically can achieve transmission accuracies of better than 0.1 %.

Absorption Coefficient

The most widely adopted method for measuring low level optical absorption losses in the infrared is adiabatic laser calorimetry. Thermocouples are attached to the sample periphery and, for a given incident laser power, the thermal rise and decay as a function of laser irradiation is recorded. The magnitude or rate of thermal rise in the sample is proportional to the absorption coefficient of the sample (both surface and bulk absorption). If the absorption coefficient of the material to be tested is small, then the following equation can be used to determine the absorption of the sample:

Eq. (6)

$$\beta = \left(\frac{mc}{P_t} \right) \left(\frac{2n}{n^2 + 1} \right) \left[\left(\frac{dT_{\text{Gain}}}{dt} \right)_T + \left| \frac{dT_{\text{Loss}}}{dt} \right|_T \right]$$

Here n = index of refraction, m = mass of the sample, c = heat capacity, P_t = power transmitted, $(dT_{\text{Gain}}/dt)_T$ = slope of the rising part of the temperature vs. time curve at the temperature

$\left. \frac{dT_{Loss}}{dt} \right|_T$ = absolute value of the slope of the falling part of the temperature vs. time curve at a temperature T , and β = fraction of the power absorbed by the sample.

For a well designed calorimeter, the sample will be sufficiently thermally isolated so that $|dT_{Loss}/dt|_T$ is small compared to $(dT_{Gain}/dt)_T$. This is accomplished by using a suitable sample holder and placing the sample in a vacuum. Care must be taken during measurements to ensure that no laser radiation hits the thermocouples directly. Therefore, provisions must be taken to terminate (absorb) the reflected (Fresnel) light from the sample surfaces. This is usually accomplished by placing the sample to be measured at an angle ($<10^\circ$) to the laser beam and trapping the reflected light by an absorbing surface located outside (or inside) the calorimeter. Direct scattering of incident radiation onto the thermocouple appears as an anomalously fast rise in temperature at the moment of laser turn-on followed by an equally sharp decay in thermocouple signal when the laser is switched off. In order for Eq. (6) to be valid, the sample must be irradiated for a sufficient time such that each point within the sample experiences the same rate of thermal rise.

Equation (6) permits calculation of the fraction of power absorbed by the sample, β . In order to calculate the bulk absorption coefficient of the optical material, α_b , one must separate the bulk and surface contributions from the measured absorption using the following equation:

Eq. (7)

$$\beta = \alpha_b L + 2\alpha_s$$

where α_b = the bulk absorption coefficient (cm^{-1}), L = the length of the sample (cm), and α_s = the absorption per surface of the sample. The standard calorimetric technique used to separate bulk and surface components is to measure the absorption as a function of sample length. A plot of β vs. L for a number of different sample lengths should produce a straight line with the slope equal to the bulk absorption coefficient and the intercept equal to twice the surface absorption. To make this measurement properly, care must be taken to ensure that all the sample surfaces are identical and have a superior optical finish. This is best accomplished by polishing all the samples to be tested at the same time under exactly the same conditions.

Much of the published data on the absorption coefficients of IR transmission materials is calculated assuming $\alpha_s = 0$. This "effective" absorption coefficient, which is just β/L , is expected to be higher than the bulk absorption coefficient in Eq. (7) because of the contribution from the surface.

Dielectric Properties

In response to numerous inquiries, Advanced Materials has assembled the following data on the dielectric properties of our infrared materials.

There are three groups of measurements reported. The first two sets were obtained at the Engineering Experiment Station (EES) of the Georgia Institute of Technology. The first set of data was obtained under a subcontract to Georgia Tech supported by Boeing Aerospace Company¹ Temperature dependant data were obtained by Dr. James Fuller, et al., under a contract with U.S. Air Force Wright Aeronautical Laboratory (AFWAL).² The third group of data at lower frequencies was obtained at the AFWAL Dayton, Ohio.³

The dielectric and loss tangent of CVD ZINC SELENIDE were measured at Georgia Tech in three mm-wave frequency bands using several different methods. The results indicate that at room temperature, the dielectric constant is about 9.0, and the loss tangent is below 0.001. As the temperature increases to 550°C, the dielectric constant increases linearly to about 10.0, and the loss tangent increases to about 0.01. Compared with ceramics such as aluminum oxide or silicon nitride, which have similar dielectric constants, zinc selenide (ZnSe) is significantly more temperature sensitive.

The 94 GHZ measurements were performed by inserting 0.05-inch thick slabs of CVD ZINC SELENIDE into a Fabry-Perot cavity resonator. This instrument is particularly well suited for samples that are available as slabs of uniform thickness.¹ Further dielectric measurements were performed on samples of ZnSe machined to fit in circular waveguide cavities. A very tight sample fit can be obtained in the circular waveguide, and resonant cavity measurements are sensitive to small loss tangents. These measurements were performed at Ka- and U-band frequencies from room temperature to 550°C, using instrumentation and techniques that have been developed under contract No. F33615-82-C-1718 with the AFWAL Avionics Laboratory (AADM-1).² Results are given in Figures 1-11 for frequencies from 28.9 to 42.4 GHz.

The frequency dependent variations in dielectric constant are repeatable, but they are believed to be due to the instrumentation rather than the ZnSe. The scatter in the loss tangent data is due to random errors in the measurement at very small quantities. The variation in properties that increase with temperature are believed to be accurately represented.

Dielectric measurements were also performed at lower frequencies for all of Advanced Materials' infrared materials: CVD ZINC SELENIDE, CVD ZINC SULFIDE, CdS, and CLEARTRAN at AFWAL.³ The data were obtained

over two frequency ranges: 0.1 and 10.0 GHz, and 9.0 to 18 GHz. The high frequency data is good only below 15 GHz. The results (including teflon calibration) are given in Figures 12-31.

References:

1. R.L. Taylor, R.F. Donadio, J.A. Fuller, T.S. Taylor and G.N. Hill, "Development of a Dual Infrared and Millimeter-Wave Aperture Antenna," work performed under Boeing Aerospace Co., P.O. CH6411, CVD TR - 025, Oct. 1983.
2. J.A. Fuller, T.S. Taylor, T.B. Elf and G.N. Hill, "Dielectric Properties of Ceramics for Millimeter-Wave Tubes," Contract No. F33615-82-C-1718, AFWAL-TR-84-1005, Feb. 1984.
3. Questions should be referred to Mr. Brian Kent, AFWAL/AAWP-3, E-O Observables Group, Phone No. (513) 255-4465/5076.

The measurements included in this document were not made directly by Advanced Materials, and questions concerning experimental detail, accuracy, etc., should be addressed to the specific performing organization.

Safe Handling Information

CVD ZINC SELENIDE and CVD ZINC SULFIDE do not present any chemical hazard in their finished form; however, their fabrication could potentially lead to generation of hazardous materials if necessary precautions are not taken.

The hazards associated with the fabrication process depend upon the specific operation; the workpiece; the abrasive system in use; and the chemical nature of any cooling and/or suspension agents added to the process water. Grinding of these materials could potentially generate zinc selenide (ZnSe), zinc sulfide (ZnS), zinc oxides (dust or fume). Loose abrasives used in the lapping and polishing of ZnSe and ZnS may contribute to airborne contamination of the work area. Wet grinding/polishing is a commonly recommended practice to minimize airborne particulates, as well as to keep the workpiece surface cool.

These materials are sensitive to high temperature. For ZnS and ZnSe, oxidation and decomposition will occur at temperature above 200°C in oxidizing atmosphere (e.g., air, oxygen, etc...) and sublimation will occur at temperature greater than about 500°C. Treatment of our lenses under elevated temperatures must be properly controlled to prevent decomposition.

CVD ZINC SELENIDE and CVD ZINC SULFIDE are incompatible with strong acids and strong bases. Cleaning of these materials using incompatible solvents will result in decomposition with the release of toxic gases such as hydrogen selenide and hydrogen sulfide.

Controls

Ventilation: If zinc selenide or zinc sulfide are machined, ground or polished, they should be done wet to suppress dust generation. The use of water on grinding operations, however, may not eliminate the need for ventilation control as water droplets can aerosolize or evaporate, leaving respirable airborne particles. Engineering controls such as local exhaust ventilation may be necessary, depending upon the degree of airborne particles being released from the operation.

Personal protective equipment: Due to the possibility of dusts and fumes being generated during the fabrication of these materials, the following personal protective equipment is recommended; depending on the degree of exposure.

- Chemical goggles, splash shields, or safety glasses to protect eyes
- Rubber gloves
- NIOSH-approved respirator, approved for toxic dusts, mists and fumes
- Eye wash and safety shower stations available in case of eye or skin contact

Care must be taken to maintain all personal protective equipment in a clean and sanitary manner. Food and beverages should be kept away from areas where zinc selenide and zinc sulfide dust may be present. Hands should be thoroughly washed before eating to prevent ingestion. Broken pieces of these materials should be treated like glass, because the material is brittle and forms sharp edges when broken.

CVD ZINC SELENIDE, CVD ZINC SULFIDE, CLEARTRAN, and TUFTRAN are trademarks of Rohm and Haas Company.

These suggestions and data are based on information we believe to be reliable. They are offered in good faith, but without guarantee, as conditions and methods of use of our products are beyond our control.

We recommend that the prospective user determine the suitability of our materials and suggestions before adopting them on a commercial scale.

Suggestions for uses of our products or the inclusion of descriptive material from patents and the citation of specific patents in this publication should not be understood as recommending the use of our products in violation of any patent or as permission or license to use any patents of the Rohm and Haas Company.



©Rohm and Haas, 2008 All rights reserved.

May 2000