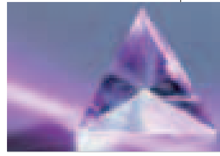
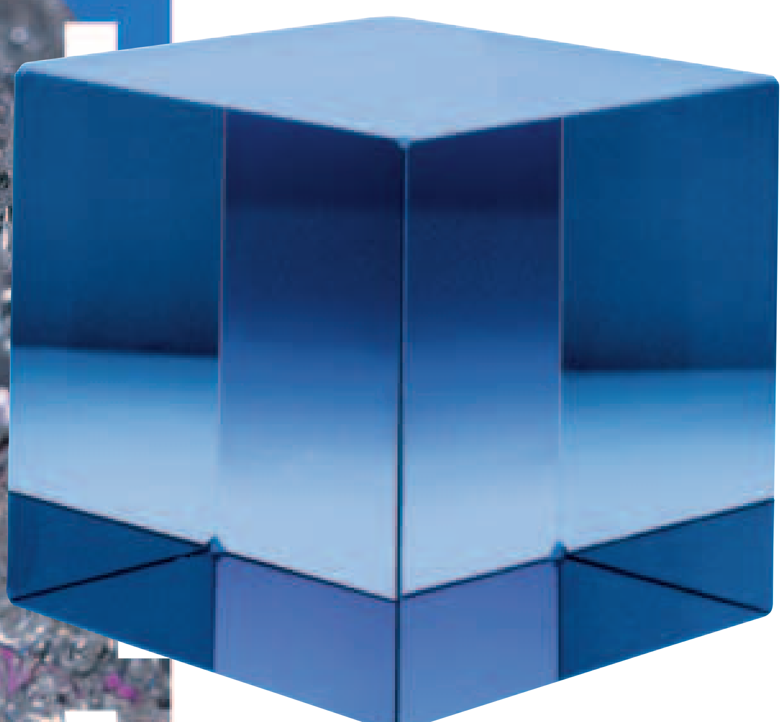
Calcium Fluoride

VUV/DUV/UV, VIS & IR applications



SCHOTT Lithotec Calcium Fluoride

Calcium fluoride single crystals, grown from high purity raw materials, are required for illumination and projection optics in 248 and 193 nm **microlithography technologies**. SCHOTT Lithotec's expertise allows fabrication of CaF_2 blanks in diameters up to 350 mm and with a thickness exceeding 100 mm and highest transmission down to 157 nm.



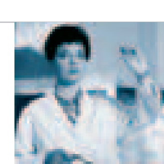
Key quality features are:

- Excellent UV transmittance
- High laser durability
- Low stress birefringence
- High refractive index homogeneity

The very high laser durability of CaF_2 makes it the first choice material for litho **excimer laser optics, beam deliveries**, and for all excimer wavelengths in a wide range of other applications.

Synthetic calcium fluoride crystals complete the application range of **optical materials** from VUV to IR with a very good transmission ranging from 130 nm to 9 µm. Advantages in optical performance can be achieved with calcium fluoride in chromatically corrected optical systems in astronomy, photography, HDTV zoom lenses, as well as in microscopy. Further applications are sensors (especially in IR spectrum), spectrometers and medical lasers.

SCHOTT Lithotec offers CaF_2 components and blanks with different crystal orientations (<111>, <100>, random or others on request) along with different surface qualities (raw, cut, ground or polished), depending on the individual requirements.



Fields of Application

IC Litho: Manufacturing Tools

Typical Dimensions:	*up to 350 mm diameter, 80 mm thickness*		
Wavelength:	*248 nm*	*193 nm*	*157 nm*
Internal Transmittance per 10 mm sample thickness [%]	*> 99.8*	*> 99.7*	*> 99.4*
Refractive Index Homogeneity PV @ 633 nm [ppm]	*1 … 15 (depending on diameter)*		
*Stress Birefringence PV @ 633 nm [nm/cm] **	*1 … 20*		
Bubbles, Inclusions (ISO 10110-3)	*1/1 x 0.063 (typical)*		

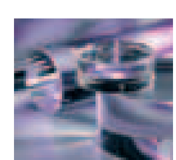
IC Litho: Excimer Laser & Beam Delivery Systems

Typical dimensions: disks - up to 100 mm diameter / 30 mm thickness; prisms - up to 100 mm edge length	
Characteristic Parameters:	*See table above: Litho Manufacturing Tools*
Laser Durability: SCHOTT Lithotec offers material with a laser durability up to highest requirements which is categorized by an internal classification method. In addition to volume characteristics, laser durability is also dependent on surface quality (with increasing laser energies) and on the laser operating conditions.	
Laser Durability Classification:	*LD-A: Superior LD-C: Advanced LD-B: High LD-D: Standard*
A qualified long-term laser durability is provided by each of these classes adapted to the individual application requirements. Please define application wavelength, energy density, repetition rate, pulse length and pulse number.	
Laser Damage Threshold @ 193 nm	*~7 J/cm^2 (effects: surface defects, ablation)*

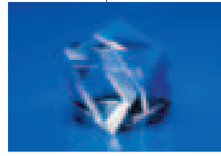
Non-Litho: Laser & Imaging Optics

Typical Dimensions: Max. dimensions:	*100 mm diameter, 30 mm thickness up to 350 mm diameter, 80 mm thickness*
Available Grades	*UV grade / 193 - 400 nm VIS grade / 400 - 780 nm IR grade / 0.78 - 6.00 µm*
Internal Transmittance per 10 mm sample thickness [%]	*> 99.0*
Refractive Index Homogeneity PV @ 633 nm [ppm]	*3 … 20*
*Stress Birefringence PV @ 633 nm [nm/cm] **	*1 … 50*
Bubbles, Inclusions (ISO 10110-3)	*1/1 x 0.10 (typical)*

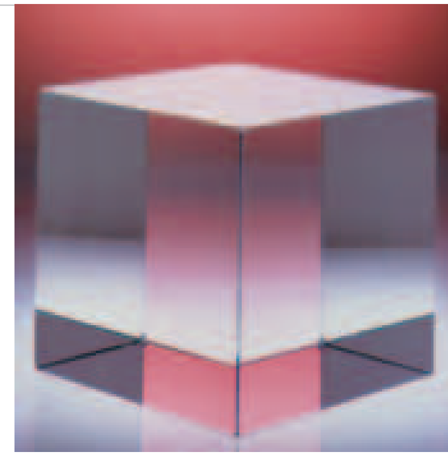
**) For single crystalline material; smallest value referring to <111> orientation. Polycrystalline material is also available.*



For other specifications and individual requirements regarding dimensions, material and surface quality please contact our sales department.
See also: Request for Quotation (advice for download on page No. 7)



Properties of Calcium Fluoride



Optical Properties

Refractive Indices $n(N_2)$ (at 22°C, nitrogen atmosphere, 1013 hPa)		
	λ_{vac}[nm]	n*
n_{2325}	2325.59	1.42212
n_{1970}	1970.56	1.42401
n_{1530}	1530.00	1.42612
n_{1060}	1060.00	1.42851
n_t	1014.25	1.42879
n_s	852.35	1.43002
n_r	706.71	1.43166
n_C	656.45	1.43245
$n_{C'}$	644.03	1.43267
$n_{He\text{-}Ne}$	632.98	1.43288
n_D	589.46	1.43380
n_d	587.73	1.43384
n_e	546.23	1.43493
n_F	486.27	1.43701
$n_{F'}$	480.13	1.43726
n_g	435.96	1.43946
n_h	404.77	1.44148
n_i	365.12	1.44488
n_{334}	334.24	1.44848
n_{312}	312.66	1.45173
n_{296}	296.82	1.45463
n_{280}	280.43	1.45824
n_{248}	248.35	1.46791
n_{194}	194.23	1.50060
n_{193}	193.37	1.50143
n_{184}	184.95	1.51055
n_{157}**	157.63	1.55927

**) Tolerances of refractive indices: $\pm 2 \cdot 10^{-5}$*
***) Measurement at NIST on 08-01-00*
All refractive indices are interpolated from values measured under dry nitrogen;
λ_{vac} = vacuum wavelength.

Relative Partial Dispersion	
$P_{s,t}$	0.2698
$P_{C,s}$	0.5333
$P_{d,C}$	0.3046
$P_{e,d}$	0.2388
$P_{g,F}$	0.5389
$P_{i,h}$	0.7462

Deviation of Relative Partial Dispersions from "Normal Line"	
$\Delta P_{C,t}$	-0.1935
$\Delta P_{C,s}$	-0.0915
$\Delta P_{F,e}$	0.0183
$\Delta P_{g,F}$	0.0552
$\Delta P_{i,g}$	0.2636

n_d = 1.43384	ν_d = 95.23	$n_F - n_C$ = 0.00456
n_e = 1.43493	ν_e = 94.69	$n_{F'} - n_{C'}$ = 0.00459

Constants of formula for dn_{abs}/dT in vacuum	
D_0	$-3.18 \cdot 10^{-5}$
D_1	$-2.31 \cdot 10^{-8}$
D_2	$4.13 \cdot 10^{-11}$
E_0	$3.35 \cdot 10^{-7}$
E_1	$1.91 \cdot 10^{-10}$
λ_{TK} [µm]	0.192

valid for 365 nm < λ < 1014 nm and for -100°C ≤ T ≤ +140°C

	Temperature coefficients of the refractive index					
	$\Delta n_{rel}/\Delta T$ [10^{-6}/K]*			$\Delta n_{abs}/\Delta T$ [10^{-6}/K]**		
wavelength [nm]	1060.0	546.23	365.12	1060.0	546.23	365.12
-40/-20 [°C]	-8.6	-8.3	-7.7	-10.5	-10.3	-9.7
+20/+40 [°C]	-10.4	-10.1	-9.5	-11.6	-11.4	-10.8
+60/+80 [°C]	-11.2	-11.0	-10.3	-12.2	-12.0	-11.3

**) relative to nitrogen*
***) relative to vacuum*

Constants of Sellmeier Dispersion Formula for λ_{vac} and $n(N_2)$	
B_1	$6.188140 \cdot 10^{-1}$
B_2	$4.198937 \cdot 10^{-1}$
B_3	3.426299
C_1	$2.759866 \cdot 10^{-3}$
C_2	$1.061251 \cdot 10^{-2}$
C_3	$1.068123 \cdot 10^{3}$

Sellmeier Dispersion Formula (according to SCHOTT Technical Information TIE29 *Literature link: 9*)
$n^2-1 = B_1 \lambda^2/(\lambda^2-C_1) + B_2 \lambda^2/(\lambda^2-C_2) + B_3 \lambda^2/(\lambda^2-C_3)$ with λ in µm

valid for 184 nm < λ < 2326 nm (22°C; 1013 hPa); $n = n(N_2)$; $\lambda = \lambda_{vac}$

Additional Properties

Chemical/Electrical Properties	
Solubility in water [g/l] 20°C	0.016
Crystal type	single crystal, synthetic
Crystal structure	cubic; CaF_2 type structure
Cleavage planes	(111)
Lattice constant [nm]	0.546342

Thermal Properties	
Melting point [°C]	1420
Mean specific heat c_p (20°–100°C) [J/(kg · K)]	854
Heat conductivity λ (20°C) [W/(m · K)]	9.71
Linear thermal Expansion coefficent	
α (20°C ; 300°C) [10^{-6}/K]	21.28
α (-30°C ; 70°C) [10^{-6}/K]	18.41

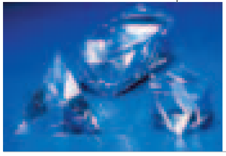
Chemical Behavior of Polished Surfaces		
Climatic Resistance Class (ISO/WD 13384)	CR	1
Acid Resistance Class (ISO 8424)	SR	4.5
Alkali Resistance Class (ISO 10629)	AR	2.3
Phosphate Resistance Class (ISO 9689)	PR	1.3
Stain Resistance Class	FR	0

Mechanical Properties	
Young's Modulus (25°C) [GPa]	75.8
Shear Modulus (25°C) [GPa]	33.77
Compressive Strength [GPa]	83.8
Poission's Ratio μ	0.26
Knoop Hardness (ISO 9385) HK	158.3
Mohs Hardness	4.0
Density ρ [g/cm³]	3.18
Grindability (ISO 12844) HG	6

Stress-Optical Coefficients $(q_{11}-q_{12})$ and q_{44} measured at NIST**

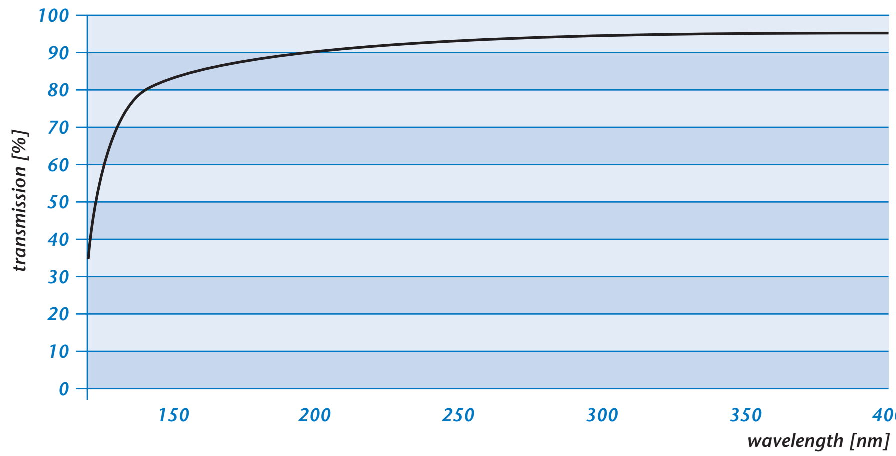
λ (nm)	CaF_2 $(q_{11}-q_{12})$ (10^{-12} Pa^{-1})	CaF_2 q_{44} (10^{-12} Pa^{-1})
637.8*	-1.46 ± 0.01	0.71 ± 0.01
546.4	-1.53 ± 0.02	0.75 ± 0.01
436.0	-1.55 ± 0.02	0.74 ± 0.01
365.1	-1.57 ± 0.02	0.74 ± 0.01
253.7	-1.66 ± 0.02	0.73 ± 0.01
193.1	-1.77 ± 0.02	0.66 ± 0.01
156.1	-1.91 ± 0.05	0.45 ± 0.01
157.63 (linear int.)	-1.90	0.46

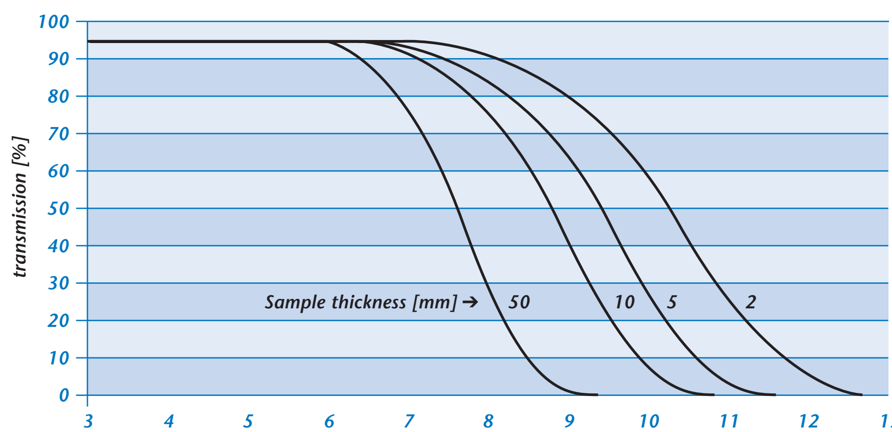
**) all values related to (111) direction*
***) Lit. 2*
For further technical information please see Lit. 1, 9, 10



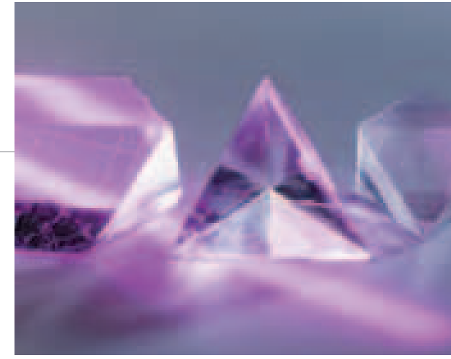
Spectral Transmission

The very broad spectral transmission range of calcium fluoride from 130 nm to 9 µm (depending on sample thickness) makes it suitable for various applications in the ultraviolet, visible and infrared spectrum.

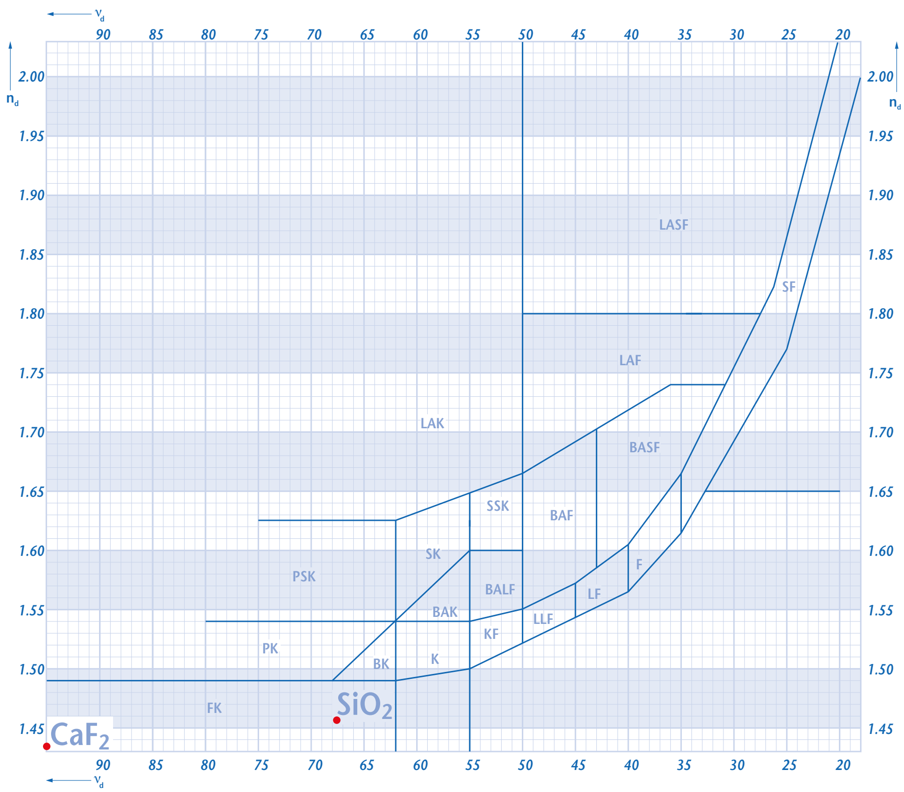




Typical transmission characteristics may vary in dependence from crystal properties



Abbe Diagram




CERTIFICATE OF APPROVAL

SCHOTT Lithotec AG
Otto-Schott-Str. 13, 07745 Jena
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DIN EN ISO 9001:2000

Development, production and sales of advanced materials and components for lithography applications.

The following downloads are available at:

http://www.schott.com/lithotec

http://www.schott.com/optics_devices

- Request for Quotation (RfQ)
- Advice for Material Handling
- Material Safety Data Sheet (MSDS)
- RoHS Statement (Restriction of Hazardous Substances)
- ISO 9001 Certificate
- Optical Glass: Description of Properties
- Technical Data Sheets (ASCII, Zemax Format)
- Abbe Diagram

SCHOTT Lithotec is certified according to ISO 9001.

List of Literature *(alphabetical)*

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3. K. Knapp, E. Mörsen, "CaF2 for 157 nm Lithography", Sematech 157 nm Tech. Data Rev., Orlando, 2001

4. M. Letz, A. Engel, W. Mannstadt, L. Parthier, U. Natura, K. Knapp, "CaF2 for DUV lens fabrication: Basic material properties and dynamic light-matter interaction", SPIE Microlithography, Santa Clara, 2004

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6. L. Parthier, G. Grabosch, U. Natura, M. Letz, K. Knapp, "ArF Immersion Lithography – a new challenge for CaF2 quality", SPIE Microlithography, Santa Clara, 2005

7. L. Parthier, Ch. Poetsch, K. Pöhl, J. Stäblein, G. Wehrhan, "Influence of lattice defects on optical homogeneity of calcium fluoride single crystals produced for high performance microlithography", presentation on DGKK, Jena, 2004 – available on request

8. K. Pöhl, L. Parthier, G. Wehrhan, J. Stäblein, "Status of the material quality of calcium fluoride single crystals produced for high performance microlithography", presentation on DUV/VUV research group meeting, Jena, 2006 – available on request

9. SCHOTT Technical Information, "Refractive index and dispersion", TIE29, Download: www.schott.com/optics_devices/english/download/

10. SCHOTT Technical Information, "Optical Glass – Description of Properties", Optical glass catalog information, Download: www.schott.com/optics_devices/english/download/

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