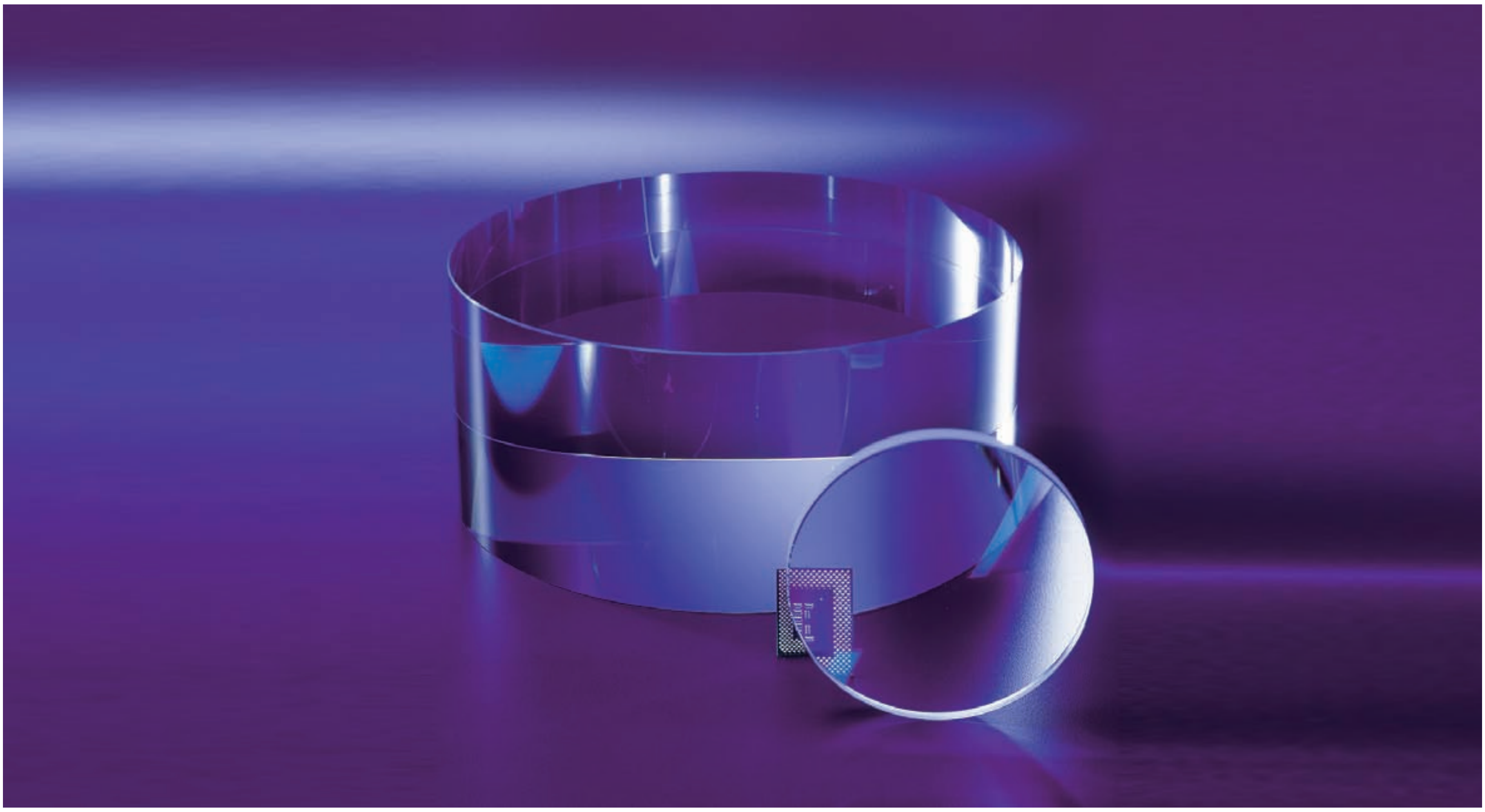
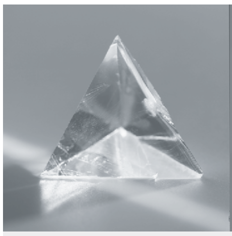
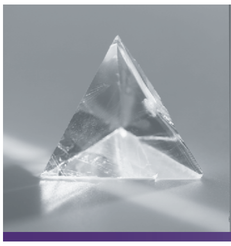




Calcium Fluoride
VUV/DUV/UV, VIS and IR applications




Lithotec Calcium Fluoride
Micro-lithography technologies

Calcium fluoride single crystals, grown from high purity raw materials, are required for illumination and projection optics in 248 and 193 nm micro-lithography technologies.

Hellma Materials' 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**

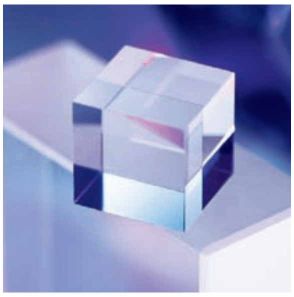
The very high laser durability of CaF_2 makes it the first choice material for litho **excimer laser optics, beam deliveries,** and for all excimer wavelengths in a wide range of other applications.

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.

Hellma Materials 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	Hellma Materials 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-B:** High **LD-C:** Advanced **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	100 mm diameter, 30 mm thickness
Max. dimensions	up to 350 mm diameter, 80 mm thickness
Available grades	**UV grade:** 193 - 400 nm **VIS grade:** 400 - 780 nm **IR grade:** 0.78 - 8.00 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 other specifications and individual requirements regarding dimensions, material and surface quality please contact our sales department.

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

Properties of Calcium Fluoride

Optical properties

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

Refractive indices $n(N_2)$ (at 22 °C, nitrogen atmosphere, 1013 hPa)			Variation over temperature
	λ_{vac}[nm]	n	$\Delta n/\Delta T\ (N_2)[1 \times 10^{-6}/K]$
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	-9.6
n_s	852.35	1.43002	-9.7
n_r	706.71	1.43166	-9.7
n_C	656.45	1.43245	-9.8
$n_{C'}$	644.03	1.43267	-9.8
n_{He-Ne}	632.98	1.43288	-9.8
n_D	589.46	1.43380	-9.8
n_d	587.73	1.43384	-9.8
n_e	546.23	1.43493	-9.8
n_F	486.27	1.43701	-9.8
$n_{F'}$	480.13	1.43726	-9.8
n_g	435.96	1.43946	-9.7
n_h	404.77	1.44148	-9.6
n_i	365.12	1.44488	-9.4
n_{334}	334.24	1.44848	-9.1
n_{312}	312.66	1.45173	-8.8
n_{296}	296.82	1.45463	-8.5
n_{280}	280.43	1.45824	-8.1
n_{248}	248.35	1.46791	-6.9
n_{194}	194.23	1.50060	-3.2
n_{193}	193.37	1.50143	-3.2
n_{184}	184.95	1.51055	-2.5
n_{157**}	157.63	1.55927	

λ_{vac} = vacuum wavelength
Tolerances of refractive indices: ±2 x 10^{-5}
** Measurement at NIST on 08-01-00. All refractive indices are interpolated from values measured under dry Nitrogen.

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

Sellmeier dispersion formula for refractive indices (λ [µm])			
$n^2 - 1 = B_1 \lambda^2/(\lambda^2 - C_1) + B_2 \lambda^2/(\lambda^2 - C_2) + B_3 \lambda^2/(\lambda^2 - C_3)$			
Constants of Sellmeier dispersion formula for λ and n (N_2)			
B_1	6.188140 x 10^{-1}	C_1	2.759866 x 10^{-3}
B_2	4.198937 x 10^{-1}	C_2	1.061251 x 10^{-2}
B_3	3.426299	C_3	1.068123 x 10^{3}

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

Refractive index variation over temperature change
$\Delta n/\Delta T$ (18 – 28 °C) = $t_0 + t_1 \cdot \lambda$ – 2 + $t_2 \cdot \lambda^{-4} + t_3 \cdot \lambda^{-6}$

Constants of formula for $\Delta n/\Delta T$ in Nitrogen		Constants of formula for $\Delta n_{abs}/\Delta T$ in vacuum	
t_o	-9.5 x 10^{-0}	D_o	-3.18 x 10^{-5}
t_1	-1.8 x 10^{-1}	D_1	-2.31 x 10^{-8}
t_2	-2.9 x 10^{-2}	D_2	-4.13 x 10^{-11}
t_3	-5.0 x 10^{-4}	E_0	-3.35 x 10^{-7}
-	-	E_1	1.91 x 10^{-10}
-	-	λ_{TK} [µm]	-

valid for 184 nm < λ < 1014 nm and for +18 °C ≤ T ≤ +28 °C

valid for 365 nm < λ < 1060 nm and for -100 °C ≤ T ≤ +140 °C

Differential temperature coefficients of the refractive index						
[nm]	$\Delta n_{rel}/\Delta T$ [10^{-6}/K]*			$\Delta n_{abs}/\Delta T$ [10^{-6}/K]**		
wavelength	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

valid for 365 nm < λ < 1060 nm and for -100 °C ≤ T ≤ +140 °C
* relative to nitrogen ** relative to vacuum

Hellma Materials
Lithotec Crystals

Properties of Calcium Fluoride
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

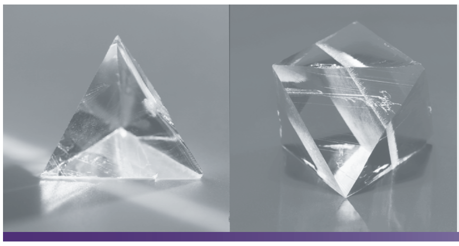
Thermal properties	
Melting point [°C]	1420
Mean specific heat $c_{p\ (20\ °–100\ °C)}$ [J/(kg · K)]	854
Heat conductivity $\lambda_{(20\ °C)}$ [W/(m · K)]	9.71
Linear thermal expansion coefficient	
$\alpha_{(20\ °C\ ;\ 300\ °C)}$ [10^{-6}/K]	21.28
$\alpha_{(-30\ °C\ ;\ 70\ °C)}$ [10^{-6}/K]	18.41
$\alpha_{(0\ –\ 25\ °C)}$ [10^{-6}/K]	18.50

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 E (25°C) [GPa]	75.8
Shear Modulus (25°C) [GPa]	33.77
Compressive Modulus K [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

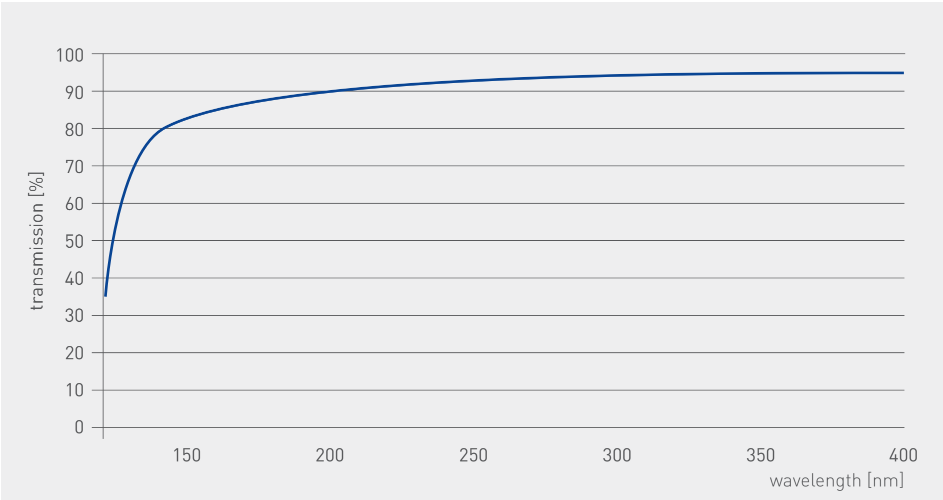
Stress-optical coefficients (q_{11}–q_{12}) and q_{44} measured at NIST**		
λ (nm)	CaF_2	
	q_{11} - q_{11} (10^{-12} Pa^{-1})	q_{44} (10^{-12} Pa^{-1})
637.8*	-1.46 ± 0.01	0.71 ± 0.01
546.4	-1.53 ± 0.02	0.75 ± 0.01
436.0	-1.55 ± 0.02	0.74 ± 0.01
365.1	-1.57 ± 0.02	0.74 ± 0.01
253.7	-1.66 ± 0.02	0.73 ± 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

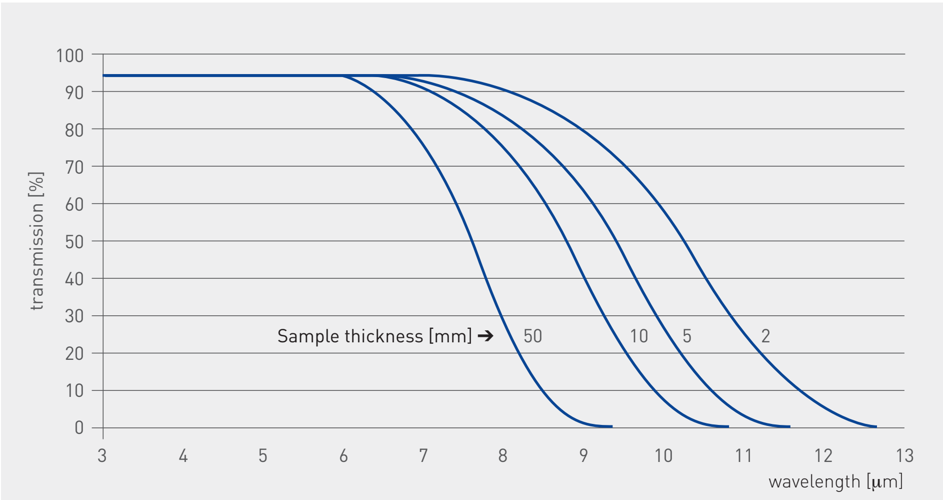
* all values related to (111) direction
** Lit. 2



Spectral Transmission

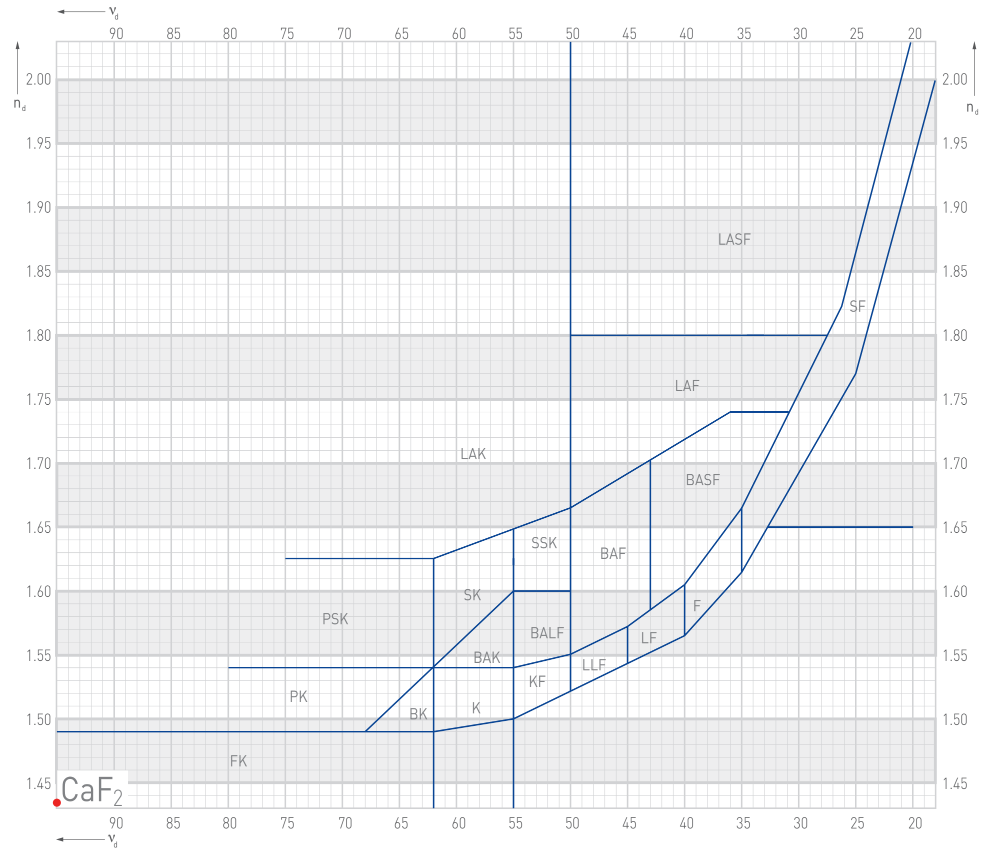
The very broad spectral transmission range of calcium fluoride from 130 nm to 9 µm (depending on sample thickness) makes it suitable for various applications in the ultraviolet, visible and infrared spectrum.





Typical transmission characteristics may vary
in dependence from crystal properties

Abbe Diagram



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Hellma Materials

Lithotec Crystals

Hellma Materials GmbH & Co. KG
Moritz-von-Rohr-Straße 1
07745 Jena / Germany
phone + 49 3641 2877 - 0
fax + 49 3641 2877 - 200
info.materials@hellma.com
www.hellma-materials.com

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