

Fluoride Coatings for the  
DUV-VUV-  
wavelength range

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**LAYERTEC**<sup>®</sup>  
OPTICAL COATINGS · OPTICS

## Outline

History:	The origin of optical coatings
Introduction:	Substrate and coating materials for the UV wavelength range Properties of fluorides Coating techniques
Examples:	Optics for Excimer Lasers Optics for Higher-harmonics Solid State Lasers Ultrafast optics for the VUV range
Summary	

## The origin of optical coatings

### Alexander Smakula (9.9.1900 - 17.05.1983)



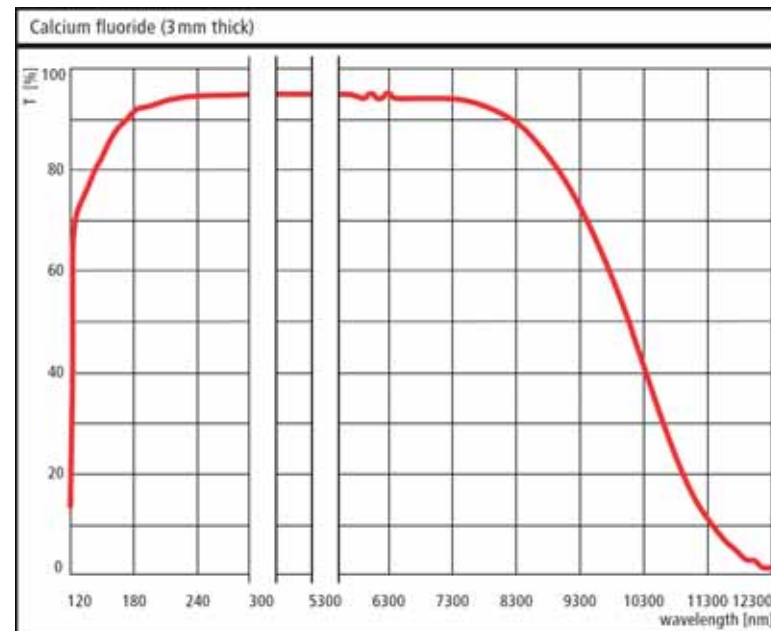
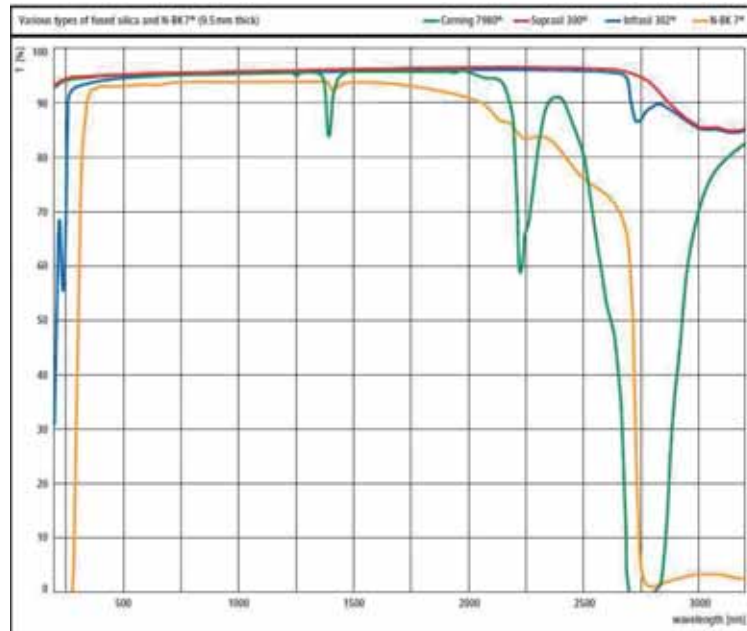
German patent No. 685 767  
on 1 November 1935



- Low index single layer coatings increase the transmittance of lenses and windows
- 1935: Kryolith ( $\text{Na}_3\text{AlF}_6$ ); ca. 1942:  $\text{MgF}_2$  on heated substrates
- Still the most popular application of fluorides
- E-beam-evaporation: 1960s , Magnetron Sputtering: 1977, IBS: 1980s

## Substrate and coating materials for the UV wavelength range

Wavelength range	materials
300-400nm	(Ta <sub>2</sub> O <sub>5</sub> ), ZrO <sub>2</sub> , HfO <sub>2</sub> , Sc <sub>2</sub> O <sub>3</sub> , Y <sub>2</sub> O <sub>3</sub> , Al <sub>2</sub> O <sub>3</sub> , SiO <sub>2</sub> , Fluorides
(190) 200-300nm	HfO <sub>2</sub> , Sc <sub>2</sub> O <sub>3</sub> , Y <sub>2</sub> O <sub>3</sub> (240-300nm), Al <sub>2</sub> O <sub>3</sub> , SiO <sub>2</sub> , Fluorides
(100) 122-200nm	SiO <sub>2</sub> (170-200nm), MgF <sub>2</sub> , LaF <sub>3</sub> , AlF <sub>3</sub> , CaF <sub>2</sub> , GdF <sub>3</sub> ...



Extremely large transmission range of fluoride materials

## Properties of fluoride materials

Fluorides = salts of fluoric acid; pure ionic bonding:

- ⇒ strong bonding of the molecules (no dissociation if evaporated)
- ⇒ weak bonding between the molecules
  - ⇒ substrates and coatings are rather soft
  - ⇒ Low melting and evaporation points (compared to oxides)
- ⇒ large coefficient of thermal expansion (CaF<sub>2</sub>: 16,7e-6/K; FS: 0,5e-6/K)
  - ⇒ thick fluoride layers on FS often crack during cool down from high deposition temperatures

Optical properties:

- ⇒ Extremely large transmission range (CaF<sub>2</sub>: ~125nm - ~8μm)
- ⇒ Small refractive indices and small refractive index contrast
  - ⇒ HR mirrors require a large number of layers
  - ⇒ Narrow reflectance bands
  - ⇒ High transmittance in the long wavelength range
  - ⇒ Relatively high scattering losses

CaF <sub>2</sub>	1,50
MgF <sub>2</sub>	1,43
AlF <sub>3</sub>	1,39
LaF <sub>3</sub>	1,66 – 1,68
SiO <sub>2</sub>	1,56

Refractive indices at 193nm

## Structure of fluoride coatings

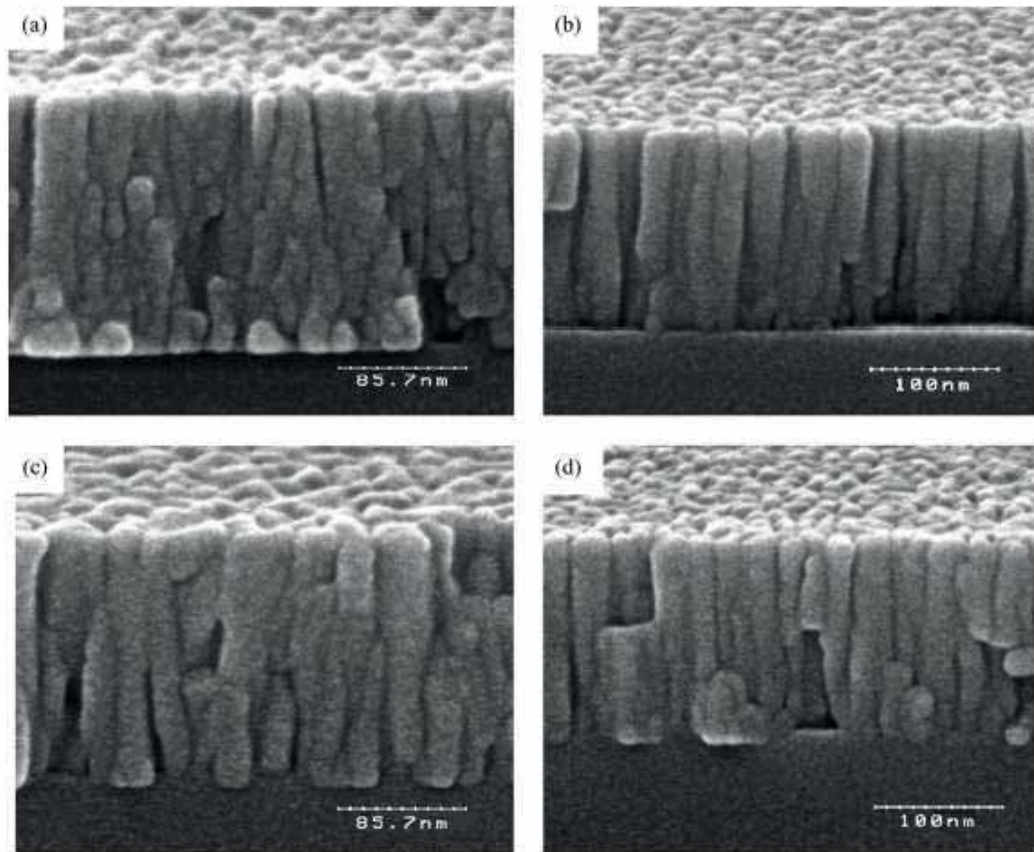


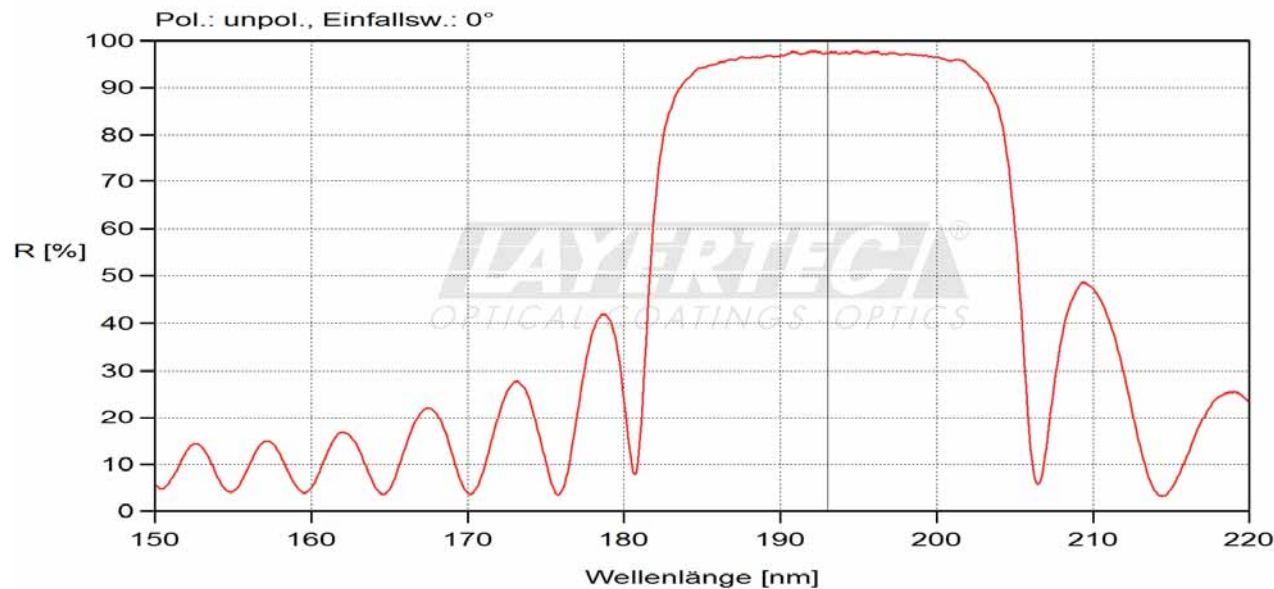
Fig. 2. Cross-sectional SEM micrographs of samples prepared at (a) room temperature at  $0.2 \text{ nm s}^{-1}$ ; (b)  $T_s = 250 \text{ °C}$  at  $0.2 \text{ nm s}^{-1}$ ; (c)  $T_s = 300 \text{ °C}$  at  $0.2 \text{ nm s}^{-1}$ ; (d)  $T_s = 250 \text{ °C}$  at  $0.8 \text{ nm s}^{-1}$ .

- Columnar structure with large voids (depending on substrate temperature and deposition rate)
- Reason of scattering losses
- Water and hydrocarbons (absorbing in the VUV!) can fill these voids
- Hydrocarbons can be removed by laser conditioning

### Coating techniques for fluoride layers

Coating technique	Advantages	Disadvantages	remarks
Thermal and E-beam evaporation	Stoichiometry of the molecules remains unchanged Low absorption High LIDT values	Dense films require high temperatures	Most common coating methods
IAD	Dense films possible Low losses at 193nm	Fluorine ! Handling and safety systems necessary! Post treatment necessary	Martin Bischoff Dissertation FSU Jena 2009 (IOF Jena)
IBS	Dense films possible Low scattering losses	NF <sub>3</sub> and Fluorine ! Handling and safety systems necessary ! Absorption losses	M. Schwarz, Veeco Presentation at AK DUV-VUV 2015-10-08, LZH

## Optics for excimer lasers: HR mirrors



### Typical reflectance values:

R > 98% at 248nm, 308nm

R > 97% at 193nm

R > 94% at 157nm

Fluorine resistant!

193.024 nm : 97.3307 %

### ArF laser mirrors (193nm); results of the German Joint Project „FLUX“, 2011

Lifetime: 10 billions of pulses at 55mJ/cm<sup>2</sup>, 4 billions of pulses at 80mJ/cm<sup>2</sup>

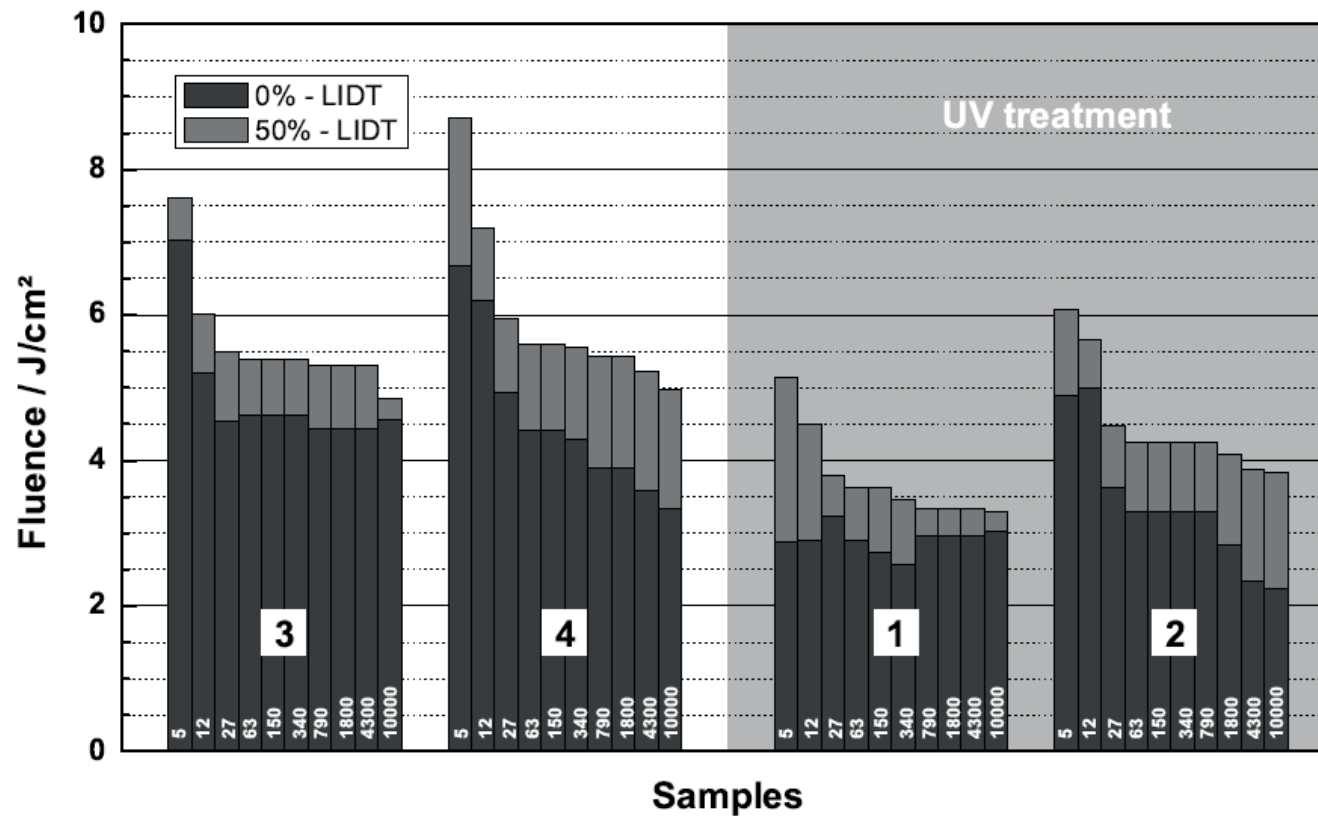
Lifetime of the optics = lifetime of the laser tube!

LIDT: 2-3 J/cm<sup>2</sup> (14ns, 10000-on-1), Measured at LZH



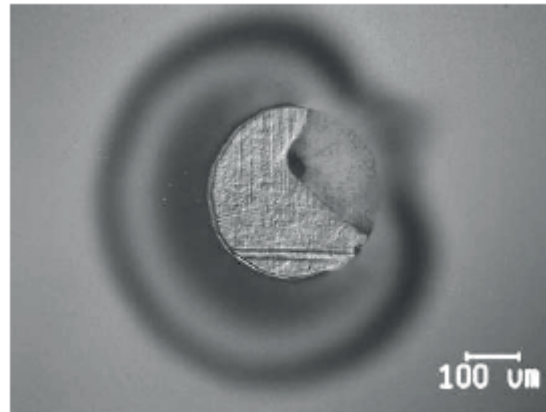
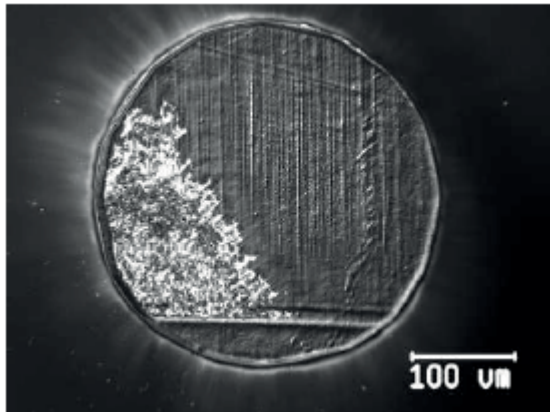
### LIDT of HR 0° 193nm vs. pulse number

$\tau=15\text{ns}$ ,  $\varnothing 350\mu\text{m}$ , 150Hz, with and without UV treatment, measured at LZH, LAYERTEC samples only

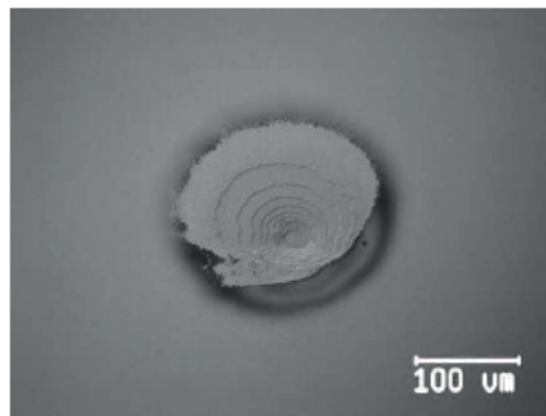


**LIDT = 2 – 3  $\text{J}/\text{cm}^2$ ,  
 relatively constant  
 even at large pulse  
 numbers**

## Damage Morphology

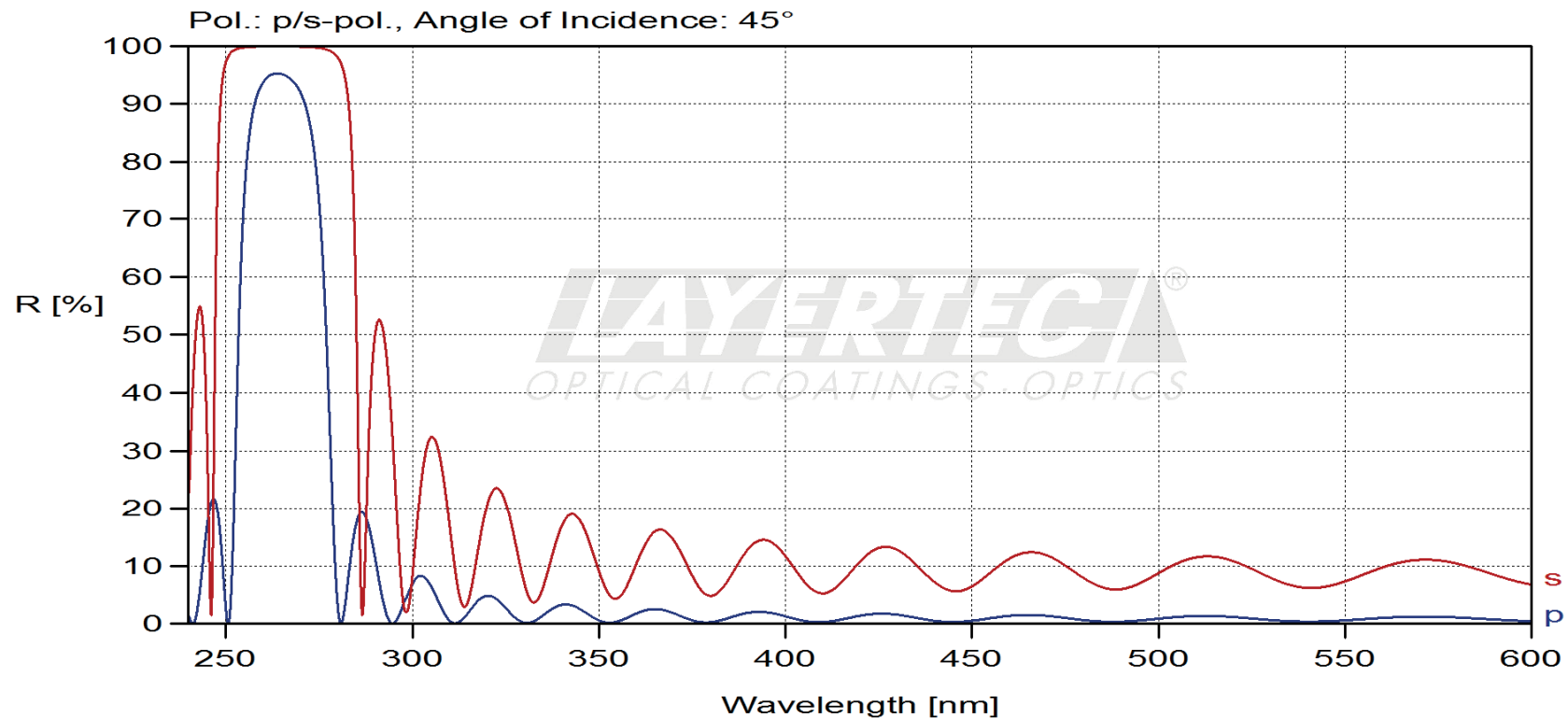


**High LIDT values:**  
Delamination;  
Damage of „the coating  
itself“



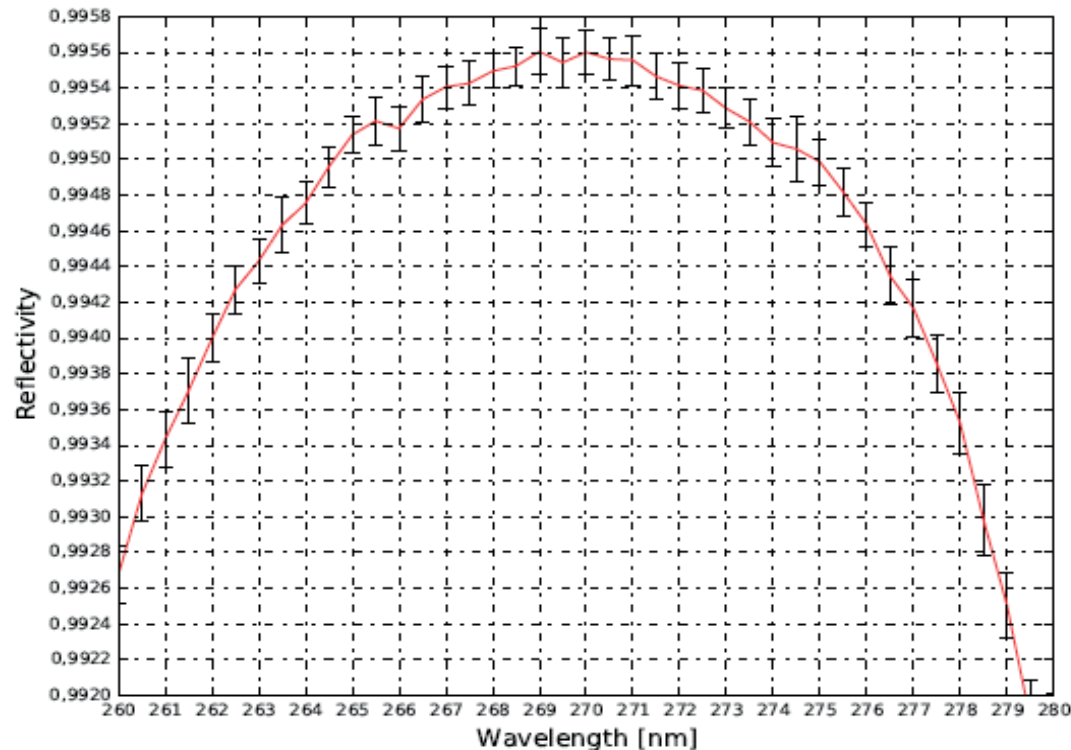
**Low LIDT values:**  
Craterlike structure;  
Driven by defects in  
the coating

**Fluoride Coatings for solid state lasers: Separator HRs 45° 266nm + HT 45° 532nm**



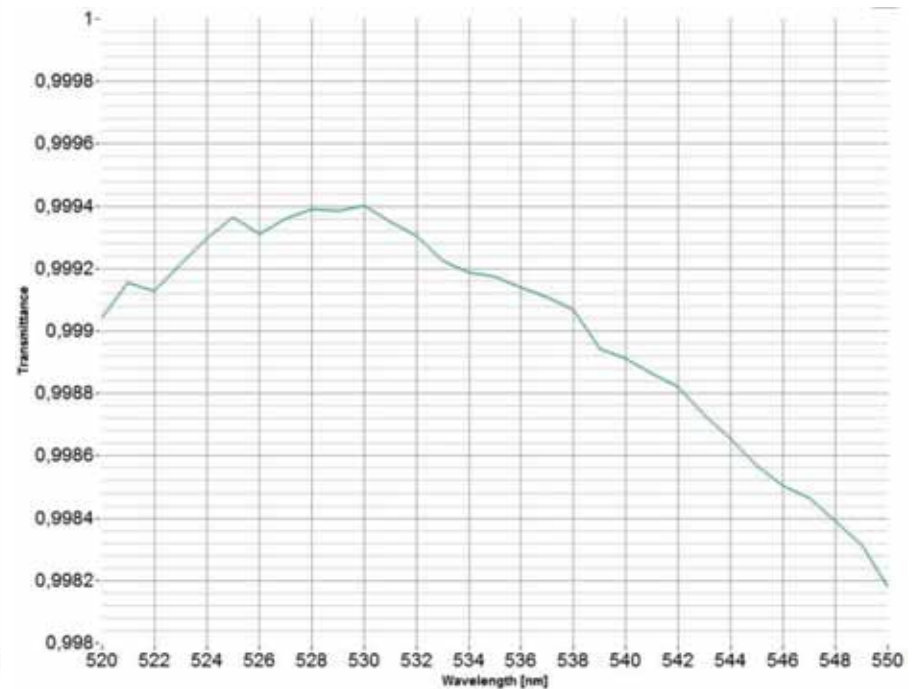
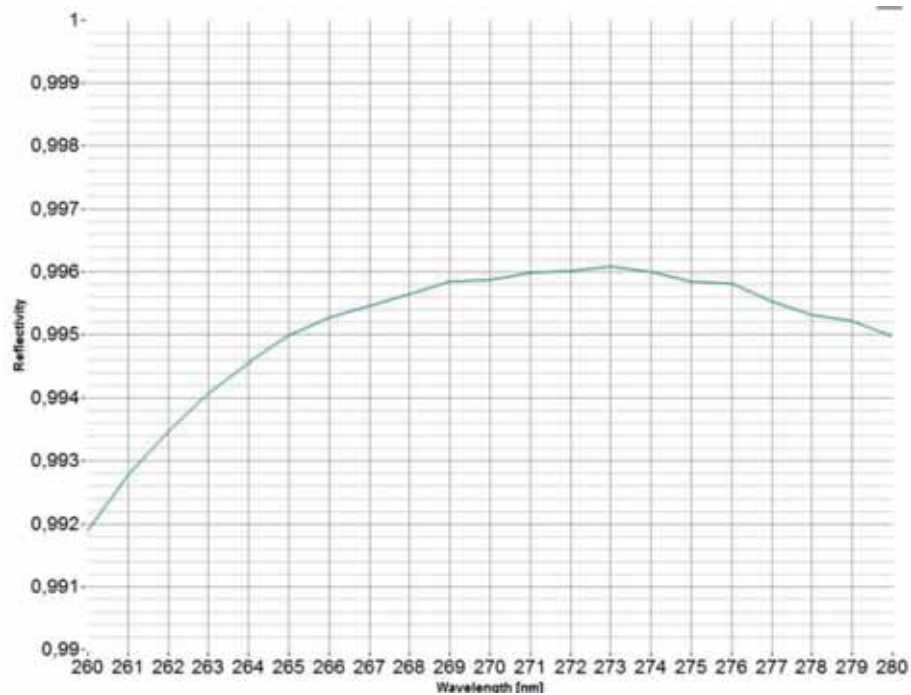
- Bandwidth of **HRs** is sufficient for spectral production tolerance of  $\pm 3\%$
- Very low reflectance in the transmittance range

**Fluoride Coatings for solid state lasers: Separator HRs 45° 266nm + HT 45° 532nm**



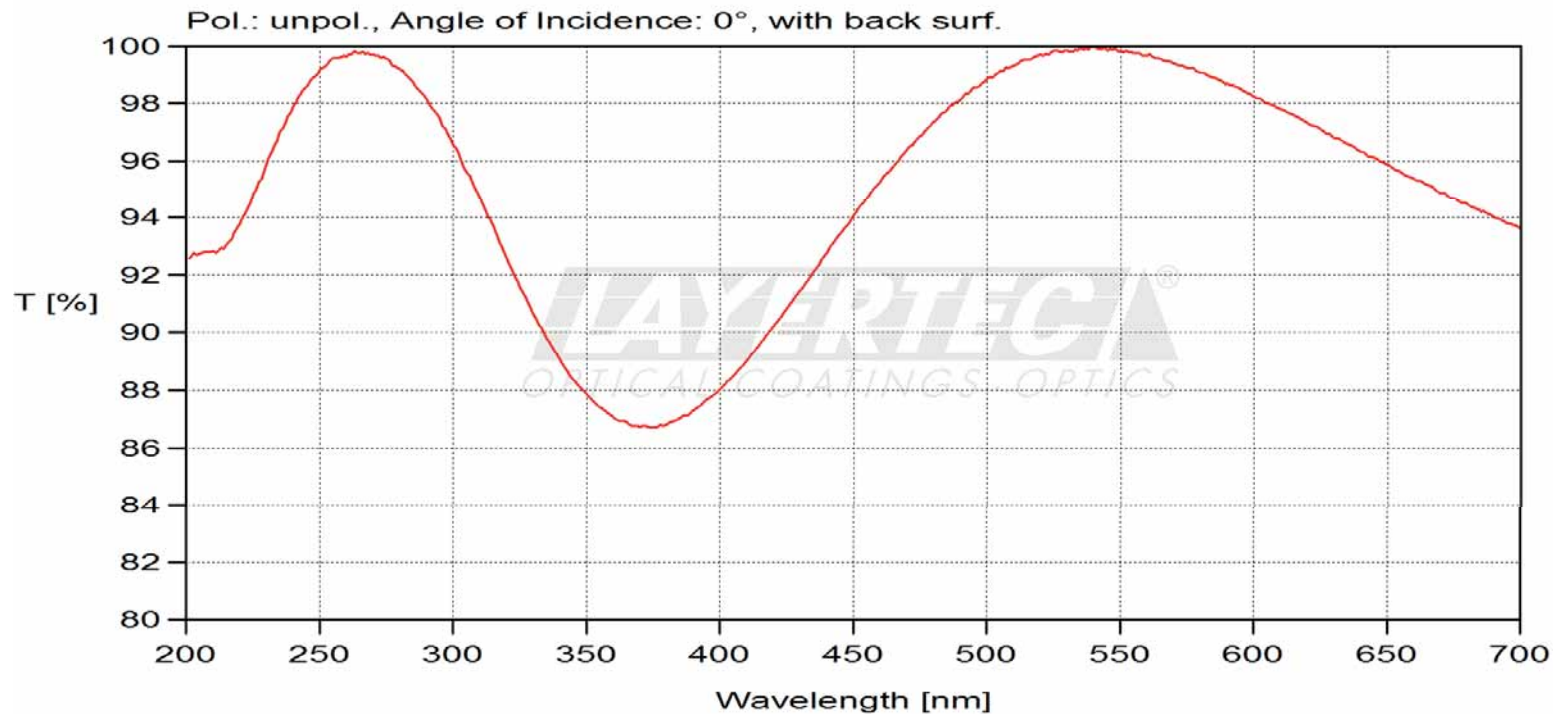
- Reflectance measurement by CRDS:  $R_s > 99.5\%$  (LAYERTEC specifies  $R_s > 98\%$ )
- $A(266 \text{ nm}) \leq 110 \text{ ppm}$  (measured by LID at IPHT Jena)
- $A(532 \text{ nm}) = 3 \text{ ppm}$  ! ( $\sim 2\mu\text{m}$  of coating material + interface!)

**Fluoride Coatings for solid state lasers: Separator HRs 55° 266nm + HTP 55° 532nm**



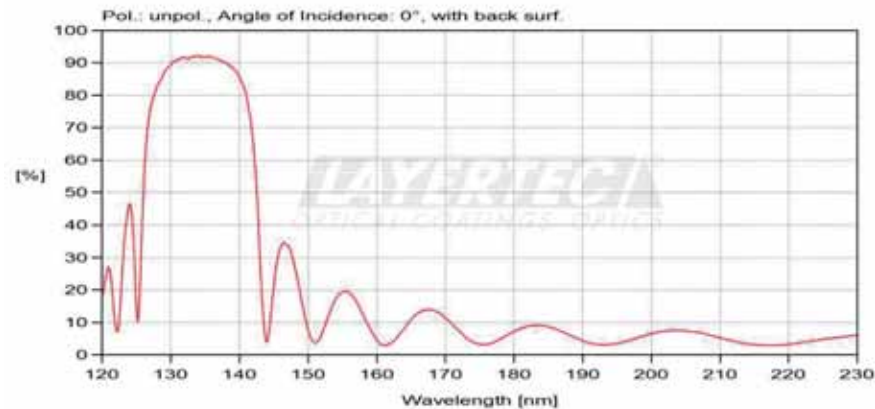
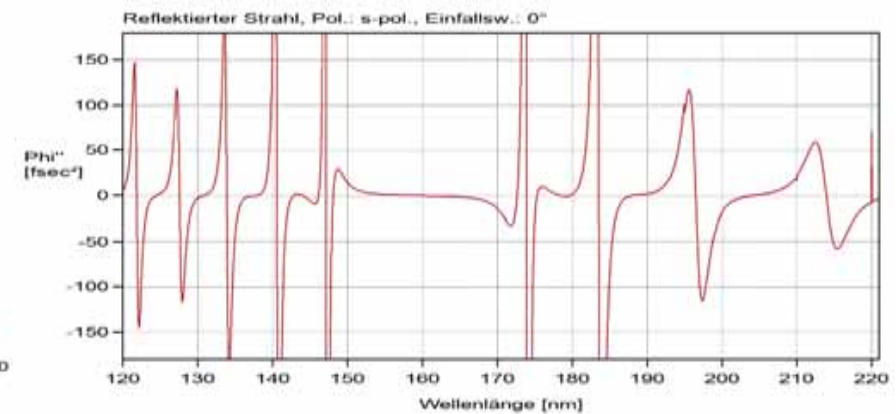
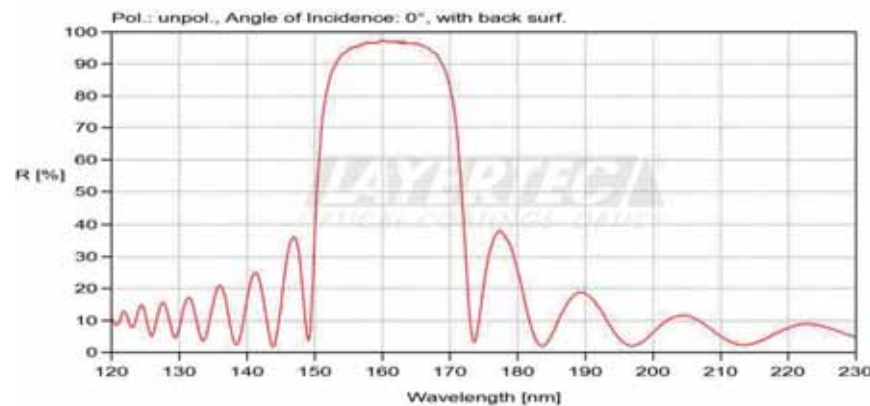
- 1-T at Brewster's angle is a nearly direct measure of the losses
- $T_p(55^\circ, 532 \text{ nm}) > 99.9\% \Rightarrow$  very low scattering losses
- Reflectance measurement by CRDS:  $R_s(55^\circ, 266 \text{ nm}) > 99.5\%$

### Fluoride Coatings for solid state lasers: DAR 0° 266nm + 532nm



- Transmittance of a window coated on both sides:  $T > 99.7\%$  (LAYERTEC specifies  $T > 99\%$ )
- $A(266 \text{ nm}) = 370 \text{ ppm}$  (measured by LID at IPHT Jena)
- $A(532 \text{ nm}) < 2.5 \text{ ppm}$

## Ultrafast mirrors for the VUV-range: higher harmonics of the Ti:Sapphir laser at 160nm and 133nm



- $|GDD| < 20fs^2$  in the reflectance band
- $R_u > 90\%$  (typically  $> 94\%$ ) at 160nm
- $R_u > 85\%$  (typically  $> 90\%$ ) at 133nm
- Mirrors and separators for  $AOI = 45^\circ$  are also possible
- Separators with  $R_s < 10\%$   $R_p < 2\%$  at 800nm / 400nm / 266nm / 200nm

## Summary

- Fluorides are the only materials for the production of laser optics for the DUV / VUV range
- Fluoride coatings for the NUV / DUV range compete with oxide coatings
  - Advantages:
    - longer lifetime
    - lower absorption losses
  - Disadvantages:
    - higher scattering losses
    - coatings are soft and can be scratched easily



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aufgrund eines Beschlusses  
des Deutschen Bundestages