High Index Materials for 193 nm and 157 nm Immersion Lithography

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Outline

- Why high index materials for immersion lithography?
  - Needed to gain benefit of high index fluids
  - Reduce lens size

- High index materials

  I. Alkaline Earth Fluorides
  - Intrinsic birefringence issue
  - Mixed solid solutions

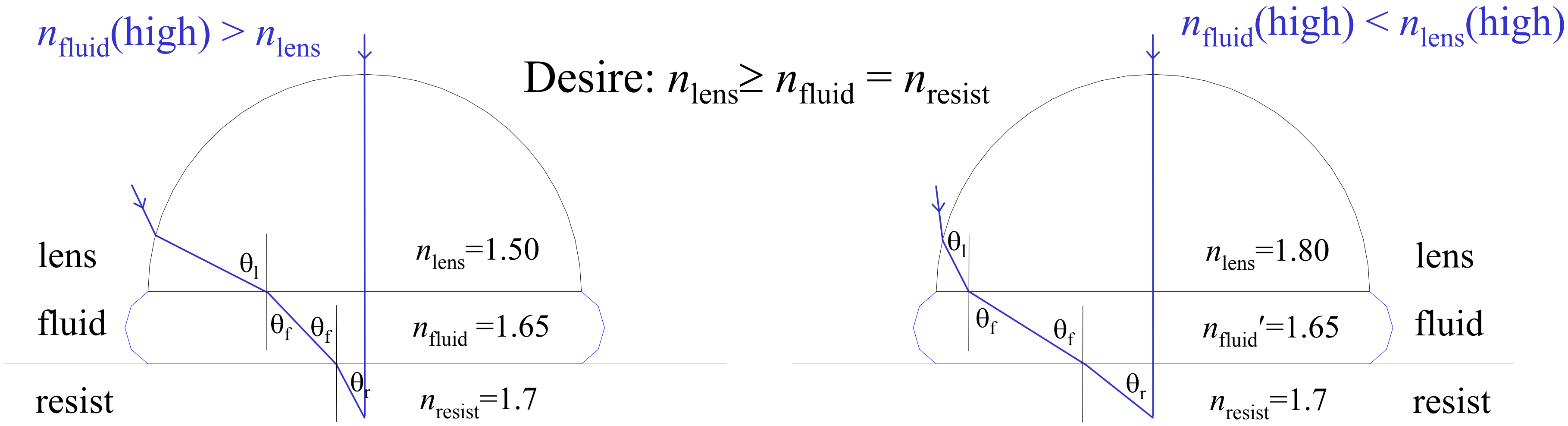
  II. Alkaline Earth Oxides

High Index Materials

Point of immersion fluid is to enable higher angles into resist ⇒ incr. NA.
Requires higher angles into the fluid from lens.

⇒ increasing size of lens to contain aberrations

If $n_{\text{fluid}} > n_{\text{lens}}$, ray bends towards normal in fluid ⇒ loose max. NA



$n_{\text{fluid}}(\text{high}) > n_{\text{lens}}$

Desire: $n_{\text{lens}} \geq n_{\text{fluid}} = n_{\text{resist}}$

$n_{\text{fluid}}(\text{high}) < n_{\text{lens}}(\text{high})$

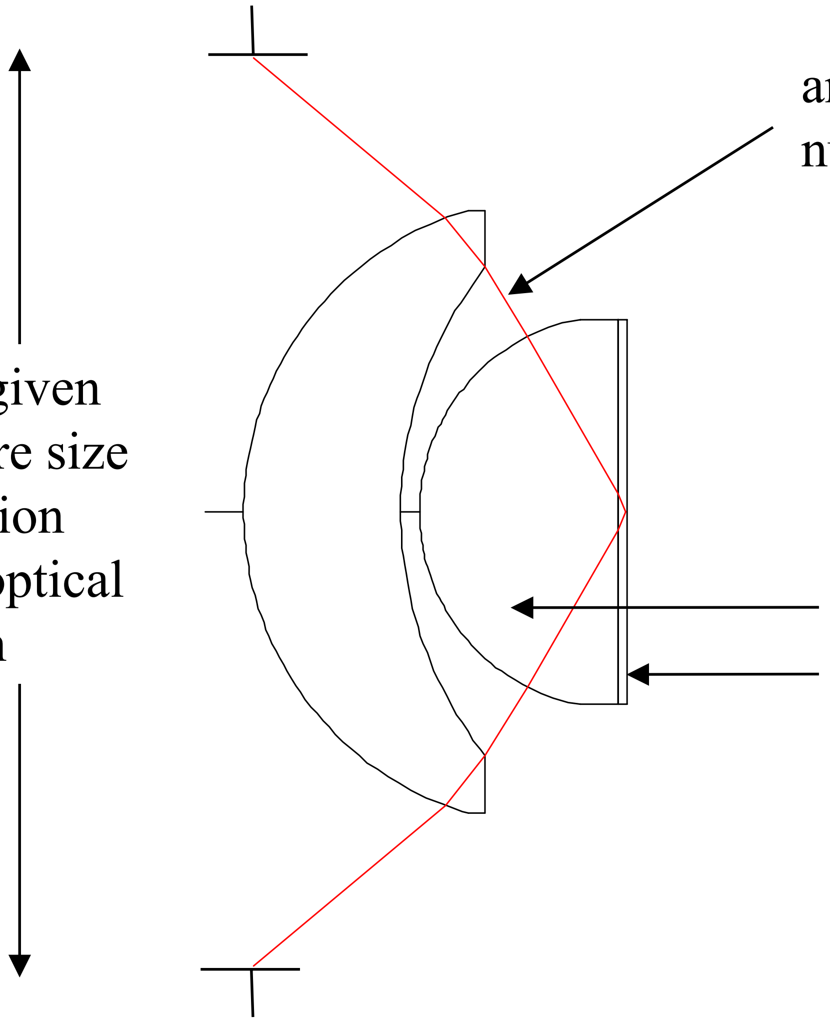
To gain full benefit of high *n* fluids need last element(s) with high *n*.
($n_{\text{lens}} > n_{\text{CaF2}}(193\text{nm}) = 1.50$)

Program to find and characterize candidate high index, isotropic (193nm transparent) materials:

Only need for last small lens element(s) ⇒ lower specs, easier to achieve

Increase System NA With Given Aperture Limit

To improve resolution with immersion fluid ⇒ larger angles ⇒ bigger optics



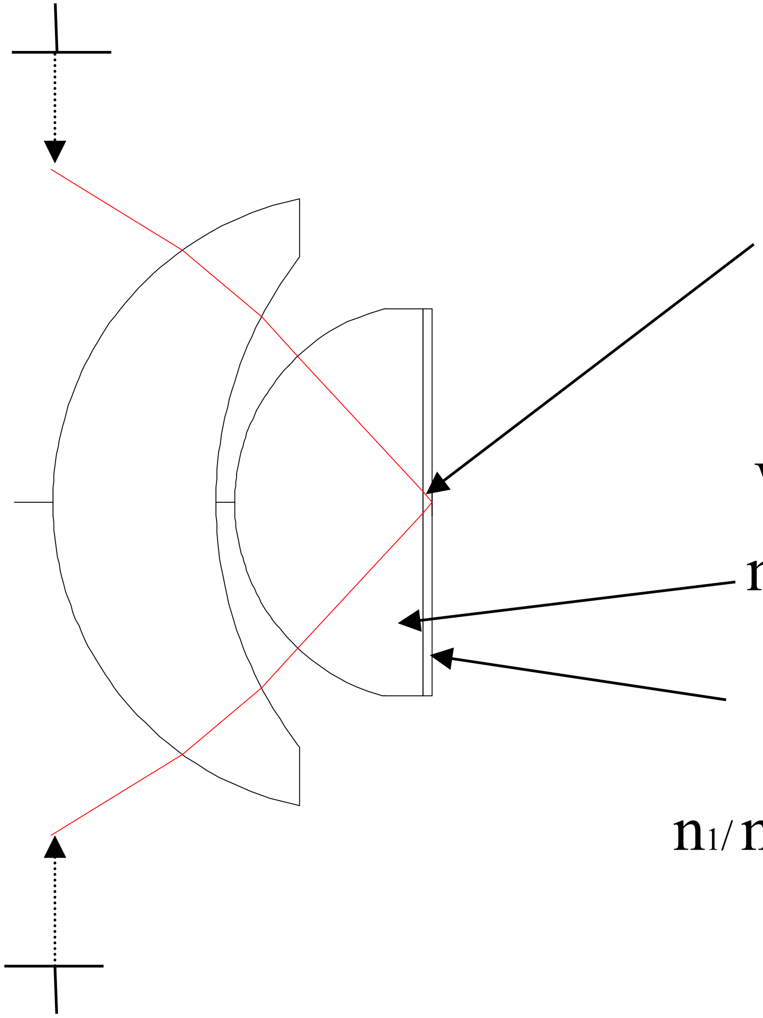
and the maximum “dry” numerical aperture

For a given aperture size limitation of an optical system

increasing the index of refraction of the the last lens together with the fluid increases the numerical aperture of the system.

Reduce Maximum Aperture With Given NA

If fluids indices are limited but even higher index materials where $n_1/n_2 >> 1.0$ can be found, then the maximum aperture is reduced



NA =1.5

Where:

$n_1 >> 1.7$ (New material)

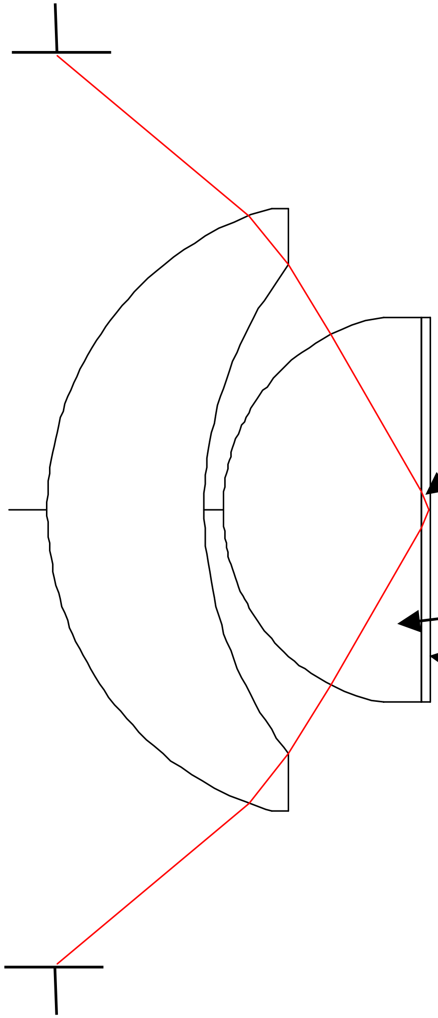
and

$n_2 \simeq 1.44$ (water)

$n_1/n_2 >> 1.0$

Reduce Polarization Effects

Ideal case:
If the fluid index and the material index are the same as the resist, index then refraction is minimized and polarization effects are reduced.



Assuming:
$n_3 = 1.7$ (resist)

NA ~1.5

Where:
$n_1 = 1.7$ (New material)
and
$n_2 = 1.7$ (New Fluid)

$n_1 / n_2 = 1.0$

High Index Materials Program

- Program to find and characterize candidate high-index UV optical materials:
  - For 193nm and 157nm

- Since would only need for last small lens element(s)
  $\Rightarrow$ specs. easier to achieve (lens small)
  lower specs. (small fraction of total lenses)

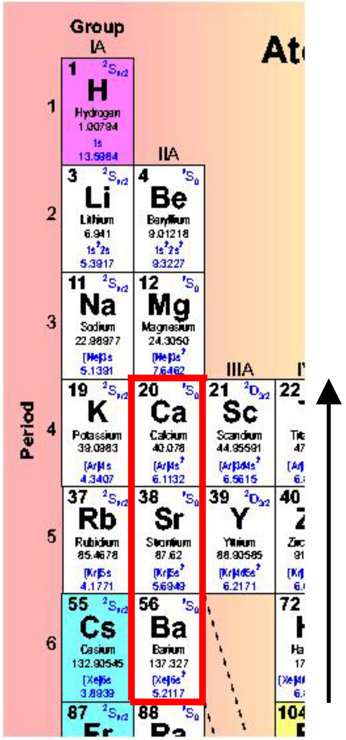
- Material requirements:
  - transparent at 193 nm (157 nm)
  - grown as large, high-quality single crystals
  - isotropic optical properties $\Rightarrow$ cubic symmetry
  - good extrinsic properties: index homogeneity, stress-induced birefringence, laser durability, …

- Must be able to contain effects of intrinsic birefringence.

Alkaline Earth Fluorides

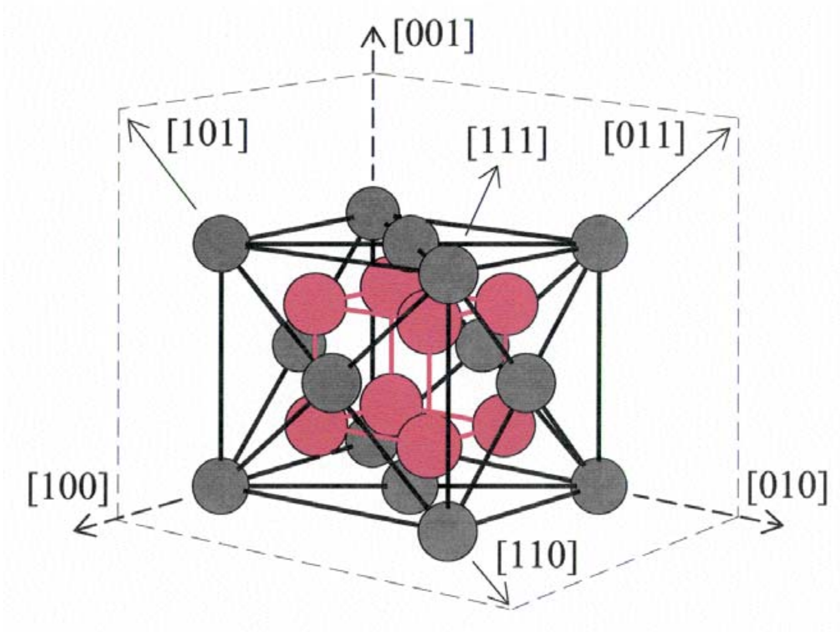
Group II Fluorides: CaF_2, SrF_2, BaF_2

- All band gap energies > 8 eV
  ⇒ all transmit at 193nm and 157 nm
- All cubic crystals: Fm3m
  (Ca on FCC lattice, F on SC Lattice)



increasing band gap energies

Material	Abs Edge	Index (193nm) (20 °C)	Index 157nm (20 °C)
CaF_2	123 nm	1.50	1.56
SrF_2	128 nm	1.51	1.58
BaF_2	134 nm	1.58	1.66



High *n* UV Optical Materials – BaF$_2$

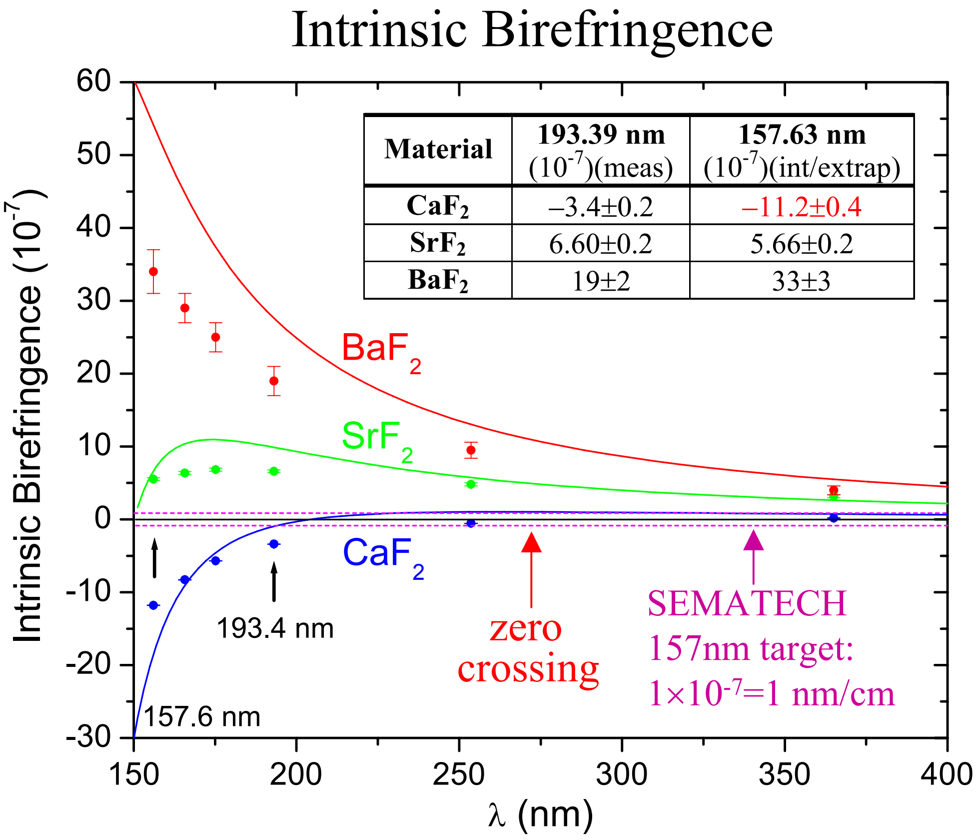
Property	**193 nm** (20 °C)	**157 nm** (20 °C)
index	1.58	1.66
dn/dλ (nm^{-1})	-0.002	-0.0044
dn/dT (°C)	1×10^{-6}	8.6×10^{-6}
q_{11} (10^{-12} Pa^{-1})	-1.7	-2.4
q_{12} (10^{-12} Pa^{-1})	2.0	2.0
q_{11} - q_{12}	-3.7	-4.4
q_{44} (10^{-12} Pa^{-1})	1..1	1.30
IBR (nm/cm)	19	33

John Burnett, “Stress Birefringence, Intrinsic Birefringence, and Index Properties of 157 nm Refractive Materials”, SEMATECH Final Report (LITJ216) (2002).

- NIST previously characterized opt. prop. – color corrector 157 nm.
- Extensive experience, BaF$_2$ brought to material specs. nearly good enough for large 157nm litho lenses (with minimal effort).
- Durable to 193 nm and 157 nm excimer radiation.
- Miscible: Ba$_x$Sr$_{1\text{-}x}$F$_2$ (all x) and Ba$_x$Ca$_{1\text{-}x}$F$_2$ near $x = 0,1$.
- Can possibly increase index (above 1.58 at 193 nm) by mixing.
- High intrinsic birefringence: 19 nm/cm (193nm), 33 nm/cm (157nm).

Eliminating Intrinsic Birefringence With Mixed Crystals

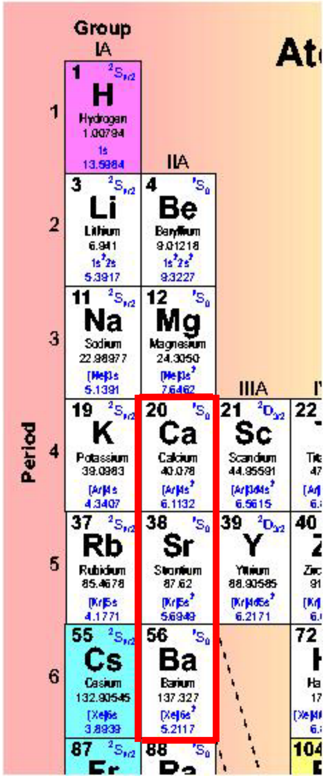
- Demonstrated CaF_2, SrF_2, BaF_2 have intrinsic birefringence and anisotropy.
- Effect governed by single parameter.



Material	193.39 nm (10^{-7})(meas)	157.63 nm (10^{-7})(int/extrap)
CaF_2	−3.4±0.2	−11.2±0.4
SrF_2	6.60±0.2	5.66±0.2
BaF_2	19±2	33±3

zero crossing

SEMATECH 157nm target: 1×10^{-7}=1 nm/cm



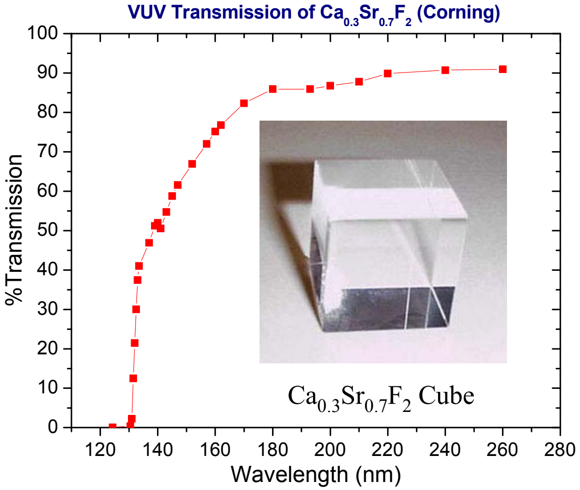
- SrF_2 and BaF_2 have IBR of opposite sign compared to CaF_2.
- Ca/Sr, and Ba/Sr miscible for all *x*, Ca/Ba miscible for some *x*.

  ⇒ value of *x* for $Ca_xSr_{1-x}F_2$ or $Ca_xBa_{1-x}F_2$ can be chose so that $\Delta n = 0$.
- Calc. $Ca_{0.3}Sr_{0.7}F_2$ nulls IBR at 157.6 nm; $Ca_{0.7}Sr_{0.3}F_2$ nulls IBR at 193.4 nm.

$Ca_xSr_{1-x}F_2$ Crystals

- $Ca_xSr_{1-x}F_2$ mixed crystals for x=0.1-0.9 grown by Corning, North Brookfield.
- Vacuum Stockbarger technique – no attempt to optimize process for x.[1]
- Key results:
  - Single crystal ingots free of gross imperfections.
  - All have high transmission at 157nm (varies monotonically with x).
  - Laser durability and induced α good.
  - Stress-induced birefringence relatively high ~ 5 nm/cm.
- Post growth anneal (2003).

- Oriented and prepared 25mm cube nominally $Ca_{0.3}Sr_{0.7}F_2$, with stress-induced birefringence ~ 0.6 nm/cm.



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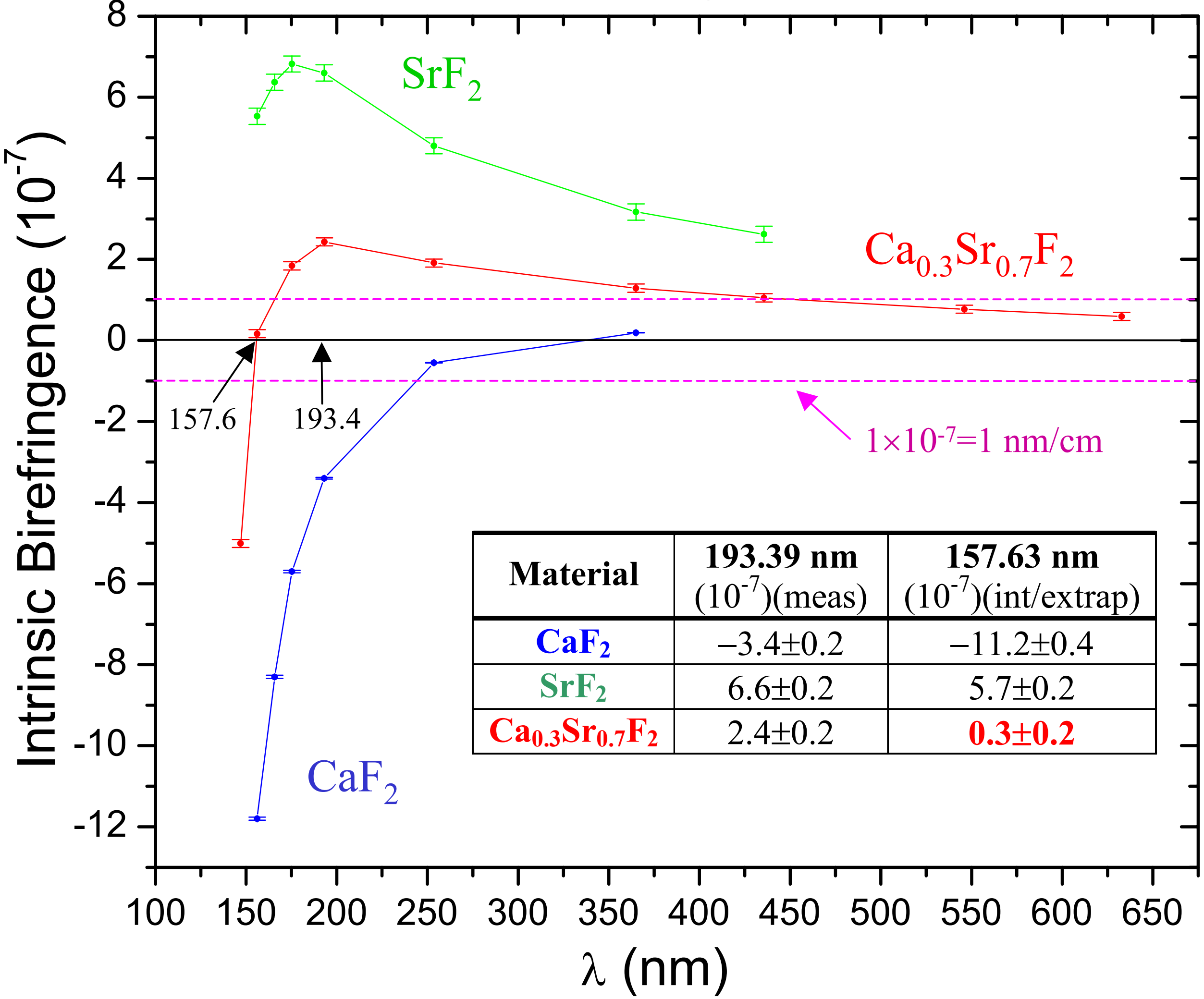
[1] C. M. Smith and R. W. Sparrow, "Optical Properties of $Ca_xSr_{1-x}F_2$ Crystals", 157 nm Symposium, Antwerp (2002).

Eliminating Intrinsic Birefringence In $Ca_xSr_{1-x}F_2$

NIST Intrinsic Birefringence Measurements



Material	**193.39 nm** (10^{-7})(meas)	**157.63 nm** (10^{-7})(int/extrap)
CaF_2	−3.4±0.2	−11.2±0.4
SrF_2	6.6±0.2	5.7±0.2
$Ca_{0.3}Sr_{0.7}F_2$	2.4±0.2	**0.3±0.2**

- $Ca_{0.3}Sr_{0.7}F_2$ eliminates intrinsic birefringence nearly completely at 157nm!
- Expect that $Ca_{0.7}Sr_{0.3}F_2$ will eliminate intrinsic birefringence at 193nm.

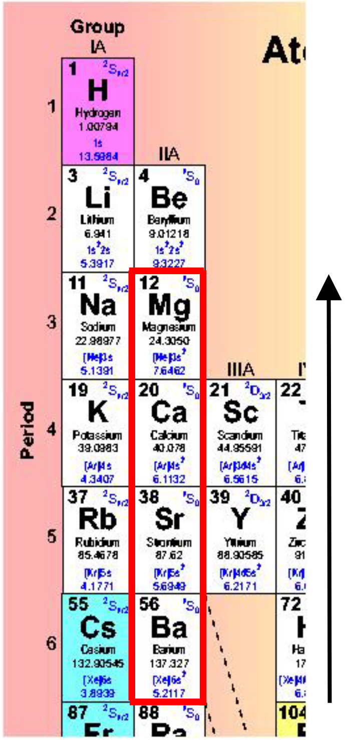
  Note: $Ca_xSr_{1-x}F_2$ does not increase *n* substantially. But,

  1) useful because incr. specs. 2) proof of principle for higher *n* materials

Alkaline Earth Oxides

Group II oxides: MgO, CaO, SrO, BaO

(Related oxides: e.g., $MgAl_2O_4$ - spinel)



increasing band gap energies

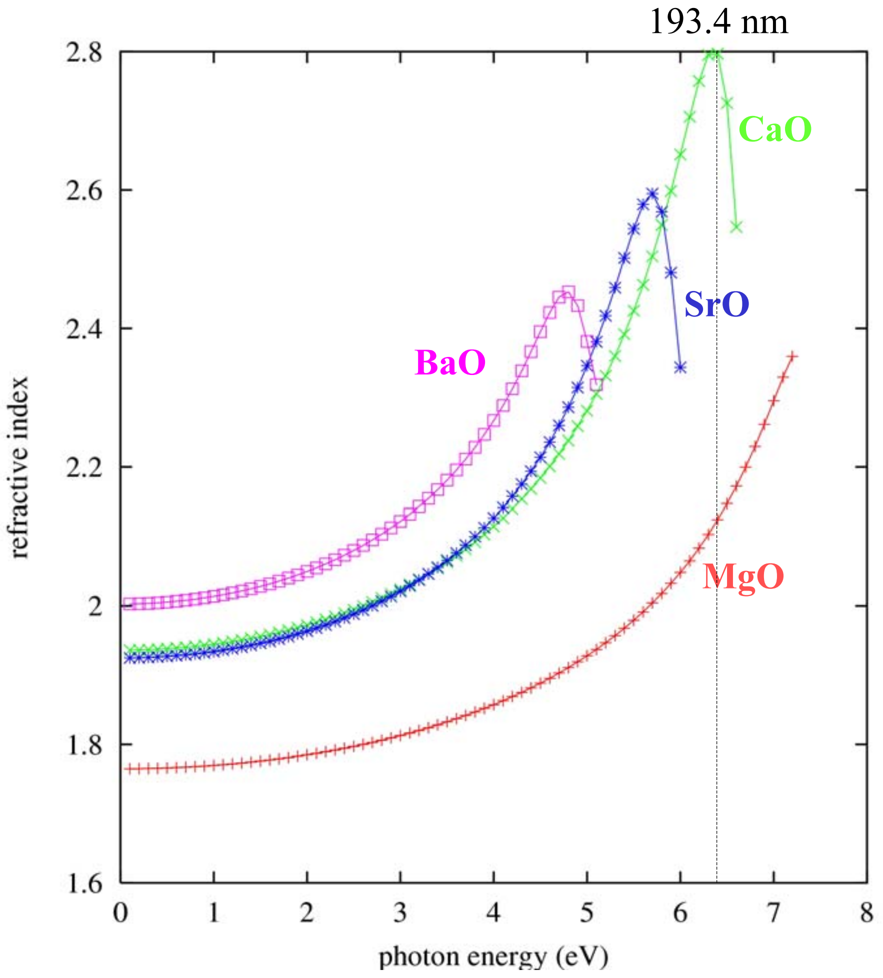
Material	Abs Edge	Index (193nm) (20 °C)
MgO	165 nm	2.0
CaO	> 200 nm	2.7
SrO	> 200 nm	
BaO	> 200 nm	
$MgAl_2O_4$	160 nm	1.8

- MgO and $MgAl_2O_4$ high transm at 193nm.
- All cubic crystals: rocksalt structure.
  (spinel – FCC)
- MgO and CaO miscible ~10%.

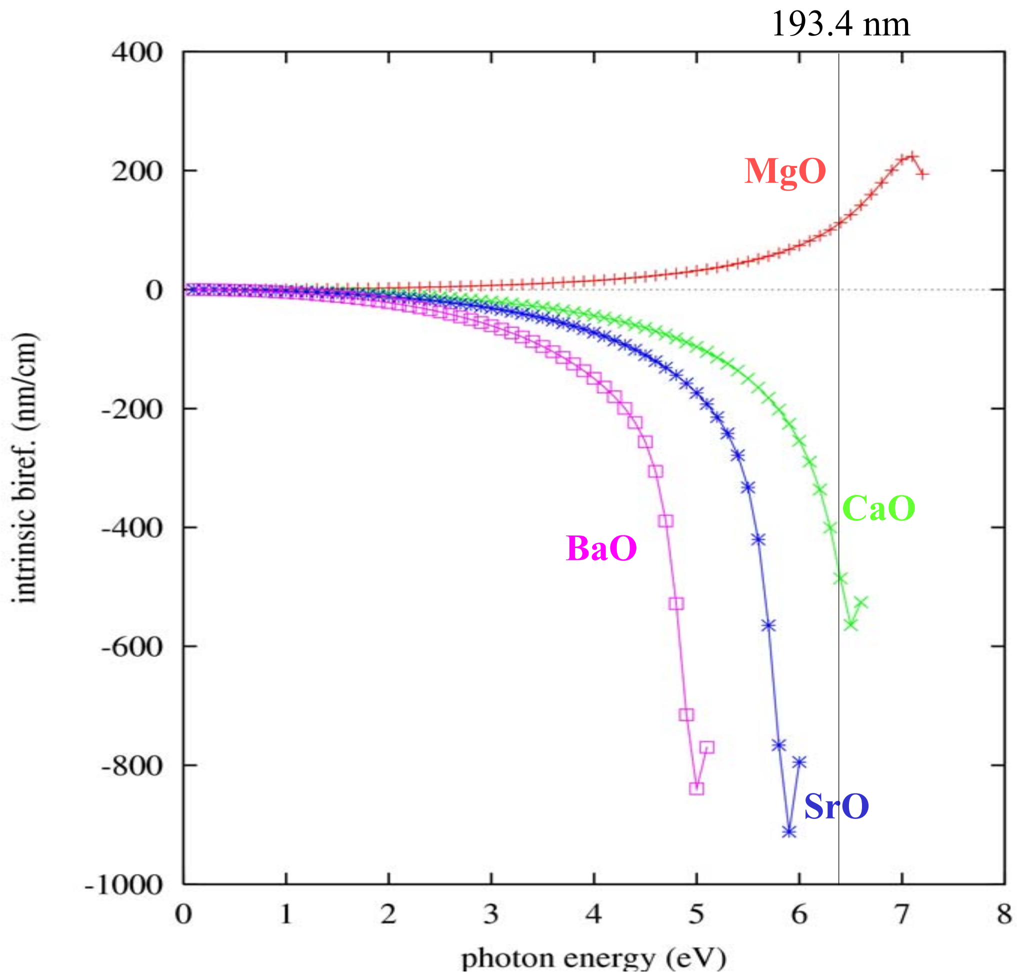
- MgO best known
  - high Tc superconductor substrate.
- Insoluble in water.
- High physical strength and stability.
- Cleaves (111) and (100) directions.
- High melting point 2852 °C.

Alkaline Earth Oxides – Calculated Dispersions

- First principles calculations (preliminary): Eric Shirley, NIST (7/13/04).
- CaO mixes with MgO to increase index above 2.0.

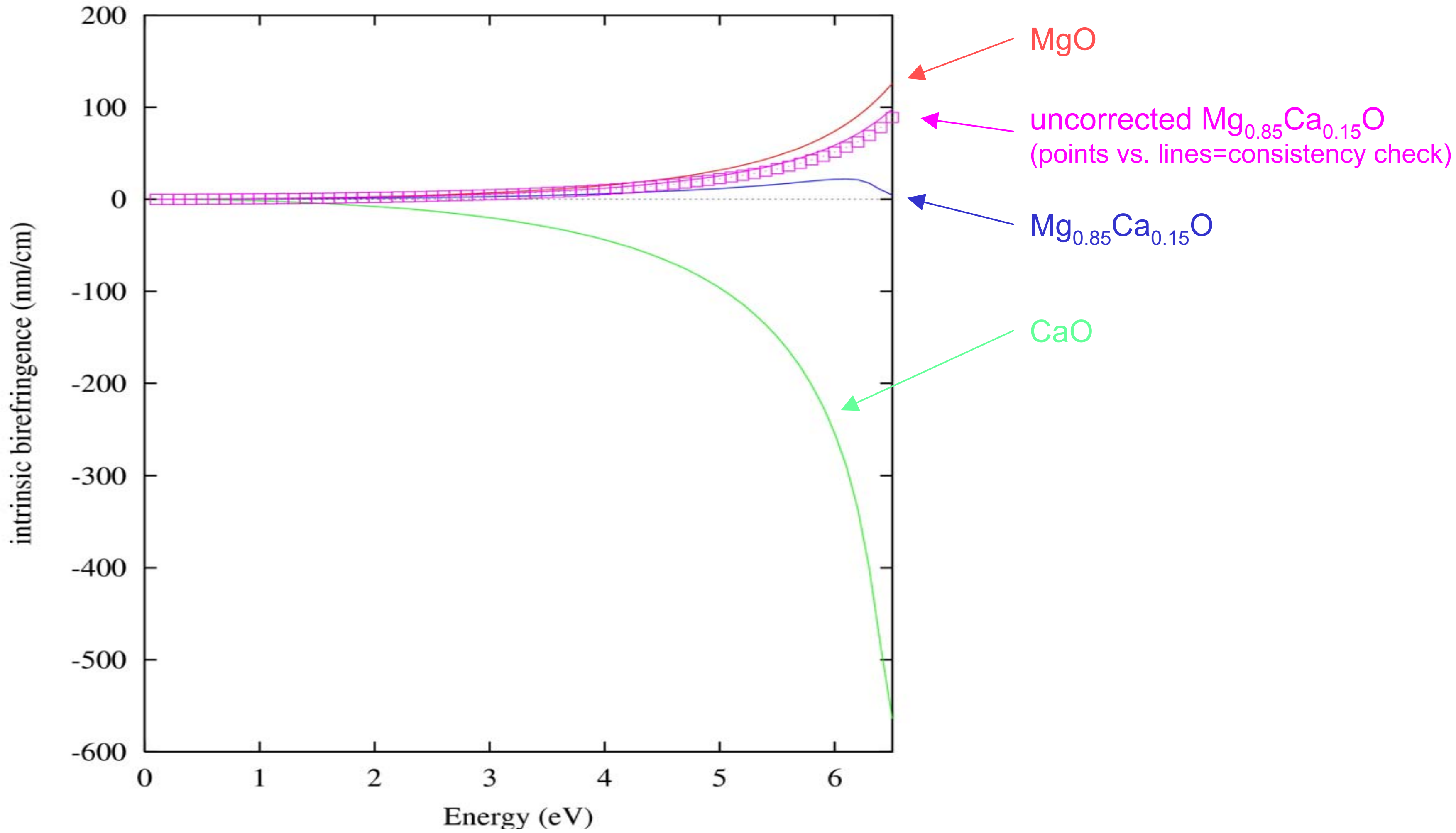


Alkaline Earth Oxides – Calculated IBR



- MgO has intrinsic birefringence opposite in sign to that of others.
- As with $Ca_xSr_{1-x}F_2$, expect can mix in small amount of CaO into MgO to get $Mg_xCa_{1-x}O$ with no intrinsic birefringence!

Simulation of IBR in MgO/CaO Mixture



- Calculations of intrinsic birefringence in $Mg_{0.85}Ca_{0.15}O$ (preliminary).
  - Indicates no intrinsic birefringence at 193.4 nm.

Conclusions

- High index materials needed for last optical element of 193 nm (157) immersion systems to gain full benefits of high index fluids.
  - enables higher NA for given aperture if you increase indices of fluid and lens material together.
  - enables smaller lens designs for a given NA.
- Some gain using BaF_2 as last element material.
- Demonstrated that mixed crystals can eliminate intrinsic birefringence in Group II fluorides ($Ca_xSr_{1-x}F_2$). Proof of principle for general case.
- More dramatic gains with MgO.
  - Mixed crystals with CaO ($Mg_xCa_{1-x}O$) should allow elimination of intrinsic birefringence problem in this material.
- These approaches require some materials research to qualify/improve materials. But the smaller (thinner) the optic, the easier to implement. Can the industry find design solutions to utilize these high index materials with small path lengths?