# High Index Fluoride Single Crystal

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Chemistry with a heart

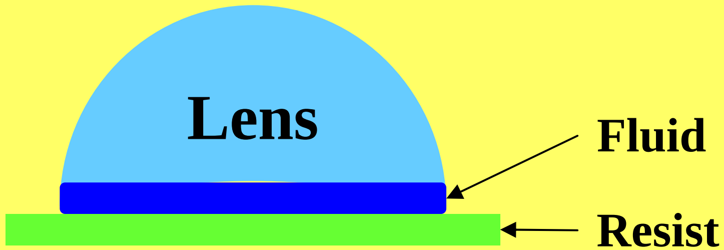
# Motivation

**High Refractive Index Material (HIM) is required for Hyper-NA 193nm Immersion Lithography in 2 Years!**

**Resolution = k1 (factor) × λ(193nm) / NA**

**NA = n × sinθ  where n : refractive index**

**'n' is restricted by minimum ($n_{lens}$, $n_{fluid}$, $n_{resist}$)**




**Candidates for HIM (our impression)**

| Required Properties | Refractive Index | Intrinsic Birefringence | Melting Point [℃] | Size (Thickness) | Transmittance / Laser Durability |
|---|---|---|---|---|---|
| Oxide crystals | High | poor | 1900~ | middle | poor |
| Oxide ceramics | High | good | - | poor | poor |
| Fluoride crystals | Low-Middle | middle | 800~1400 | good | good? |

# Concept of Tokuyama

- **Core Technology**
  - Czochralski Method
  - Large Diameter
  - Fluoride Single Crystal

Original CZ Furnace

Φ300mm $CaF_2$ Single Crystal

- **Goal**
  - Develop High Index Fluoride Single Crystal

**$BaLiF_3$($n_{193}$=1.64) Φ150 × > t50 <100>**

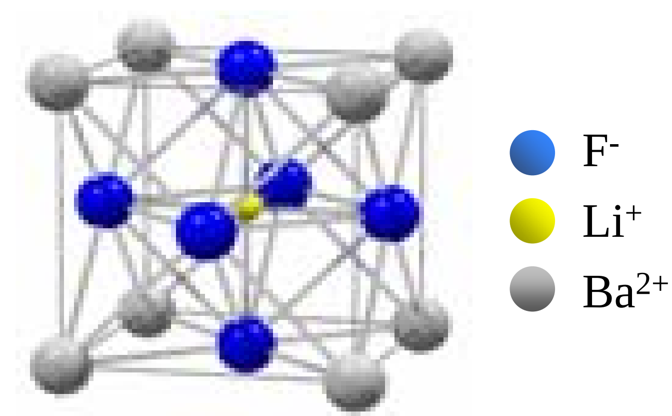
  - Develop Large Diameter <100> $CaF_2$ for IBR Compensation

**$CaF_2$ Φ300×> t50 <100>**

# Basic Property of $BaLiF_3$

| | $CaF_2$ | LiF | $BaF_2$ | $BaLiF_3$ |
|---|---|---|---|---|
| Crystal structure | cubic | cubic | cubic | cubic |
| Lattice constant [Å ] | 5.462 | 4.028 | 6.196 | 3.995 |
| Melting point [℃] | 1460 | 870 | 1355 | 880 |
| Density [g/cm$^3$] | 3.18 | 2.64 | 4.89 | 5.28 |
| Refractive Index @193nm | 1.50 | 1.44 | 1.58 | **1.64** |
| IBR @193nm [nm/cm] | -3.4 | n.a. | 19.0 | **25.4** |

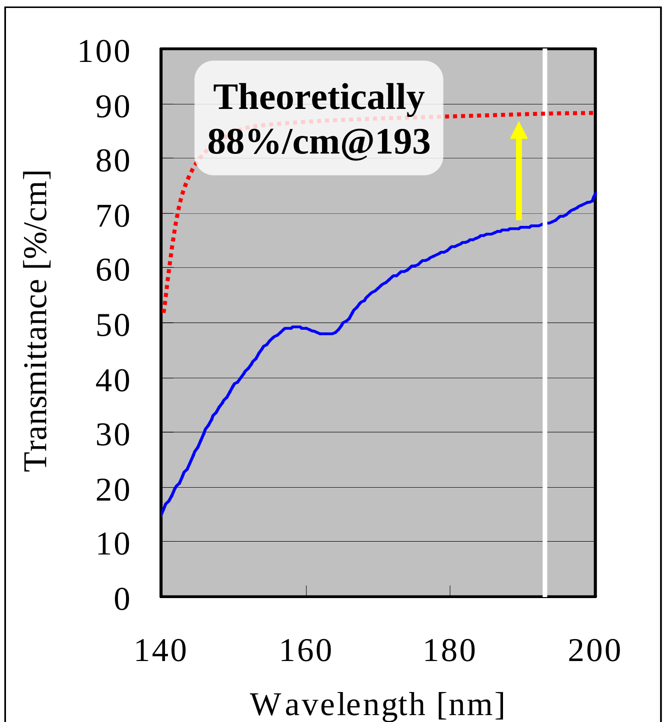
**$BaLiF_3$ < 100 > φ120×t100**




$BaLiF_3$

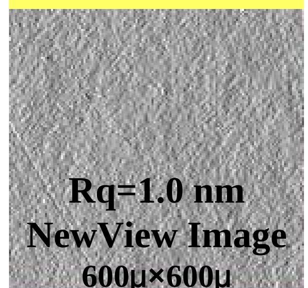
# Status and Issue of $BaLiF_3$ as of SPIE2006

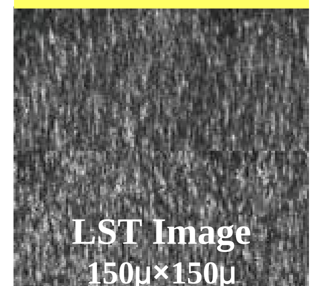
| | Orient -ation | Refractive Index | IBR [nm/cm] | dn/dt | $A_{10}$ [1/cm] | SBR [nm/cm] | HG(-Z36) [ppb] | Size [mm] |
|---|---|---|---|---|---|---|---|---|
| Target | <100> | >1.7 | <10 | | <0.01 | <1 | | φ150×t50 |
| $BaLiF_3$ | <100> | 1.64 | +25.4 | $-2.3\times10^{-5}$ | ~ 0.15 | 0.6 | n.a. | φ120×t100 |
| $CaF_2$ | <100> | 1.50 | -3.4 | $-2.9\times10^{-5}$ | 0.0005 | 0.6 | 20-40 | φ250×t50 |




※without surface compensation

**Surface Scattering** + **Internal Scattering** + **Absorption**

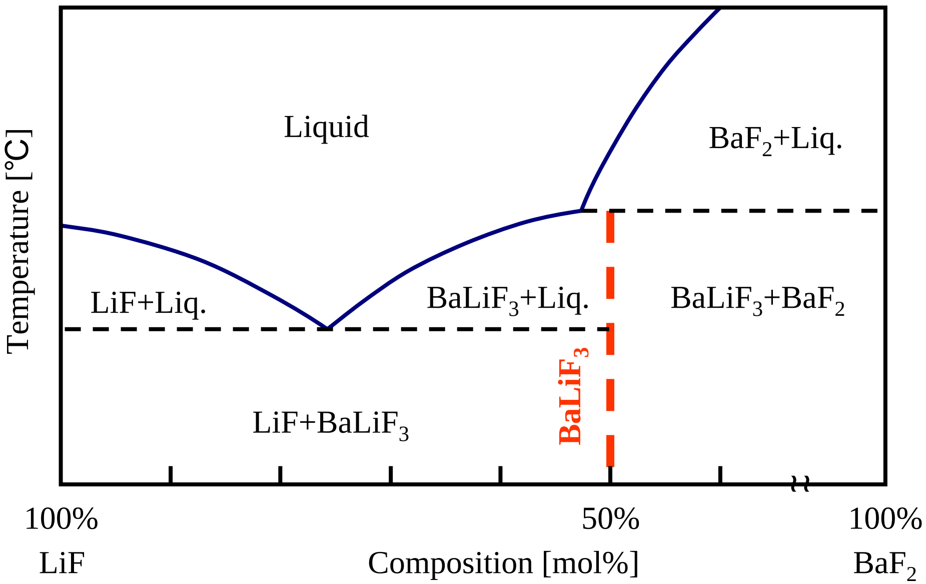



**Optimal Polishing** | **SC Elimination** | **Raw material Purification**

# Results of Crystal Growth by CZ method

Phase diagram




**$BaLiF_3$ melts incongruently!**
**⇒ It can not be grown from stoichiometric melt composition.**

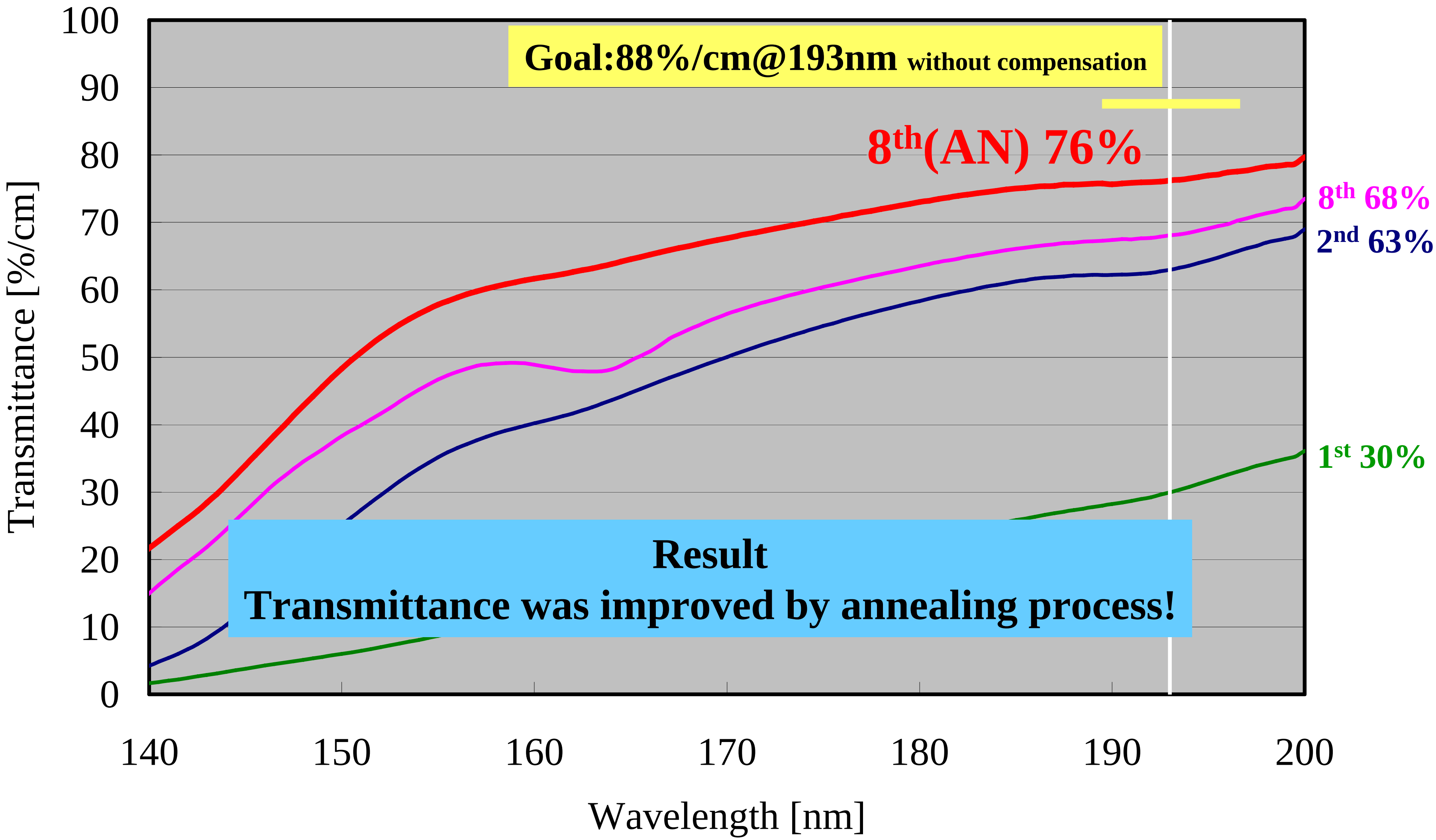
| Melt comp. Li:Ba | Obtained crystal |
|---|---|
| 50:50 | Never eutectic |
| 53:47 | Partial eutectic |
| 55:45 | Relatively clear |
| **57:43** | **Milky ~Clear** |

| Growth Condition |  |  |
|---|---|---|
| Pulling speed [mm/hr] | 1.0 →2.0 | **1.0 → 0.5** |
| Cooling rate [hr] | 60 | **4** |

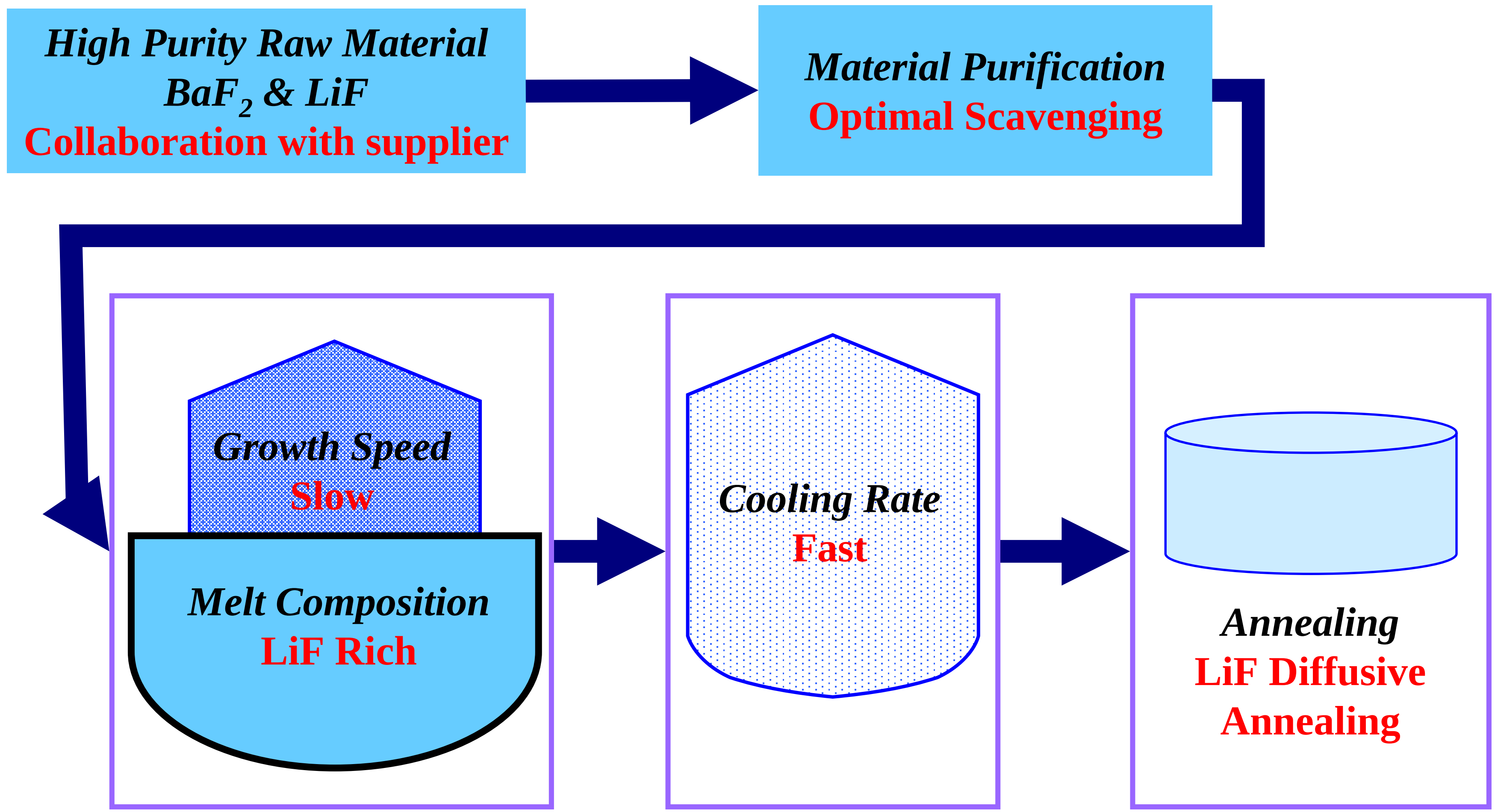
## Results

**Melt composition :Li Rich**
**Pulling speed: Slow**
**Cooling rate: Fast**

# VUV profile as of Litho Forum 2006

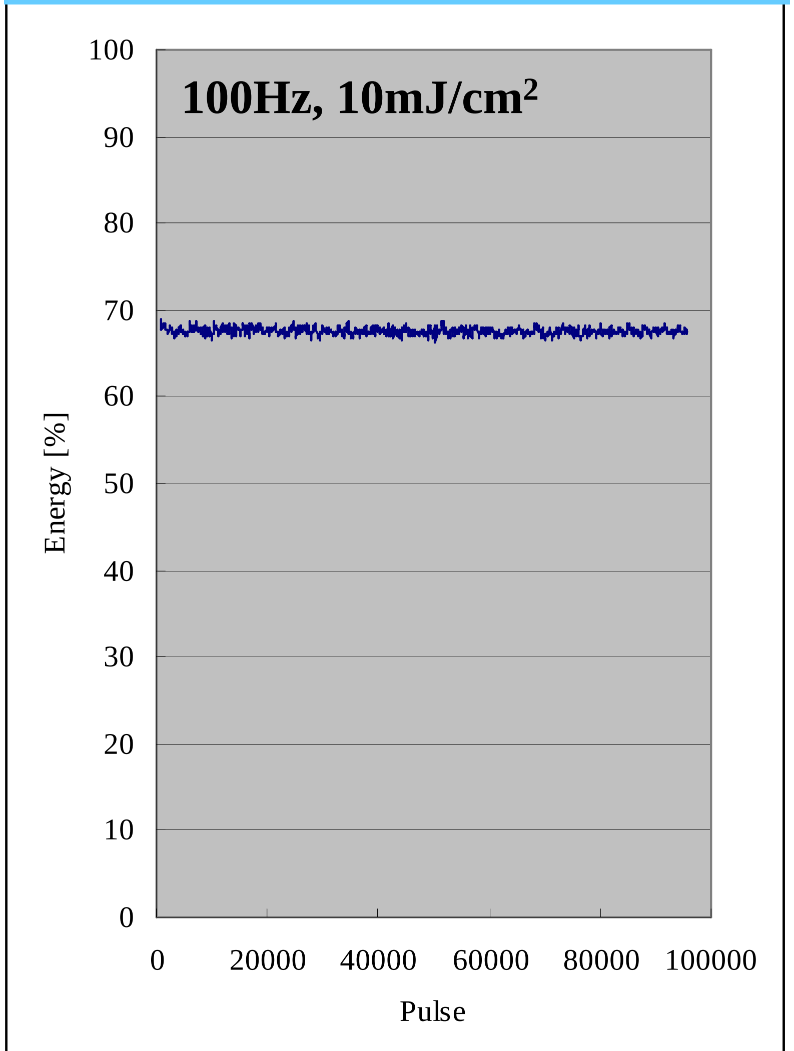


# Development Concept for Transmittance Improvement

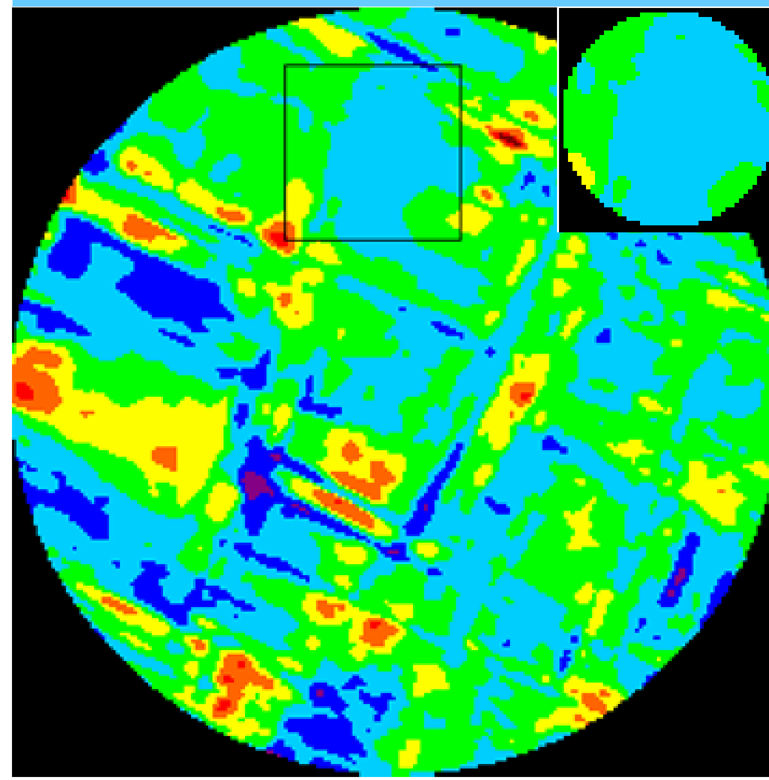


# Some Preliminary Results

## Laser Durability with ArF Laser




## Index Homogeneity (-Z36)

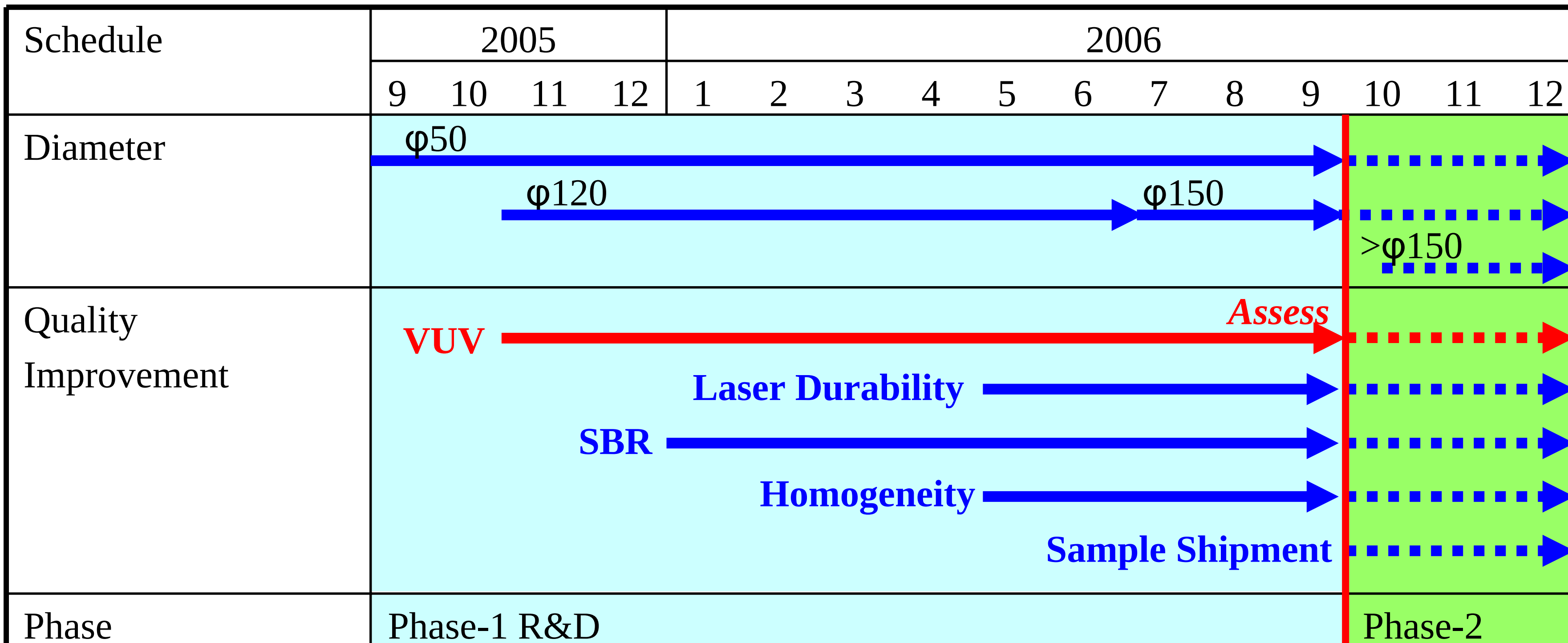


**$\Delta n_{\varphi 45}$ PV=16ppm rms=1.7ppm**

**$\Delta n_{\varphi 10}$ PV=4.9ppm rms=0.8ppm**

# Optical Property Up-date & Schedule

| | Orient -ation | Refractive Index | IBR [nm/cm] | dn/dt | $A_{10}$ [1/cm] | SBR [nm/cm] | HG(-Z36) [ppm] | Size [mm] |
|---|---|---|---|---|---|---|---|---|
| Target | <100> | >1.7 | <10 | | <0.01 | <1 | 0.02 | φ150×t50 |
| $BaLiF_3$ | <100> | 1.64 | +25.4 | $-2.3\times10^{-5}$ | ***0.067*** | 0.6 | ***~1*** | φ120×t100 |



# Conclusion

- Tokuyama try to manufacture $BaLiF_3$ as HIM and large <100> $CaF_2$ for IBR compensation.
- Critical issue of $BaLiF_3$ is transmittance.
  Champion: 0.067 [1/cm] / 85 [%/cm] *Compensated data
- Cause of transmittance debasement might be mainly due to scattering of LiF precipitation.
- Transmittance could be improved by way of optimal growth condition and special annealing process.
- Tokuyama will try to improve transmittance and assess possibility of $BaLiF_3$ by the end of September.

# Acknowledgement

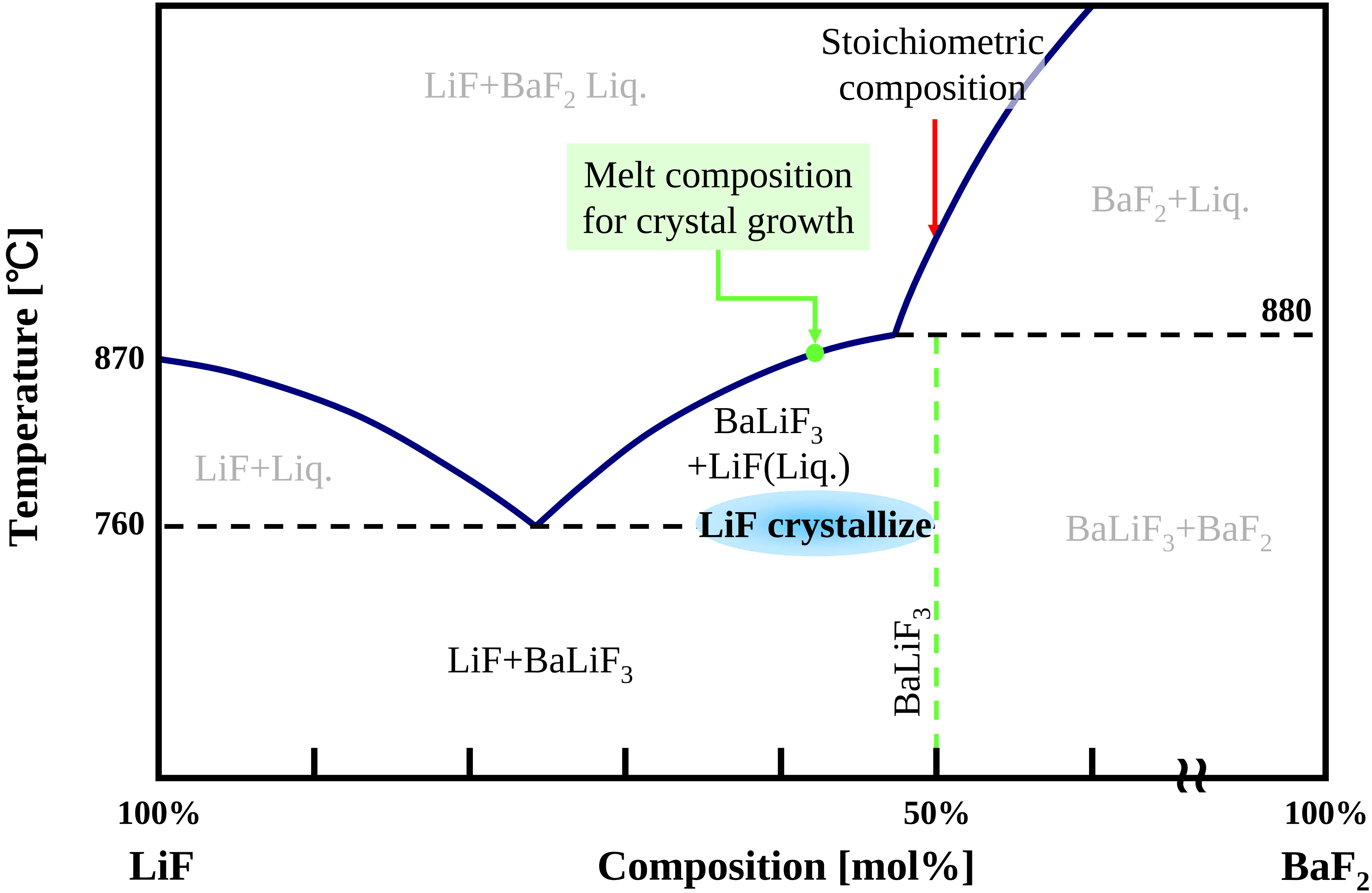

- Dr. John H. Burnet
  National Institute of Standards and Technology (NIST)
  *Evaluation (refractive index and IBR) of our samples and helpful comments.*
- All of my colleagues
  Tokuyama Corporation
  *Extreme efforts!*

# Why don't you get into the water?

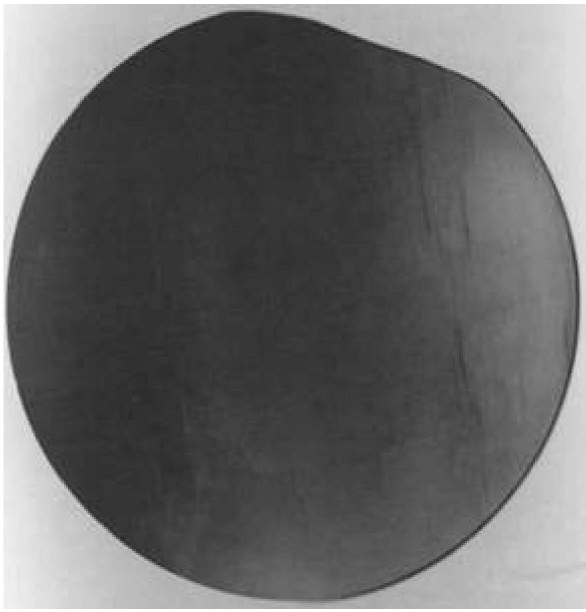

See you in Kyoto!

# Appendix

# Crystallization mechanism of $BaLiF_3$



# X-ray topography images



**$BaLiF_3$ by CZ**

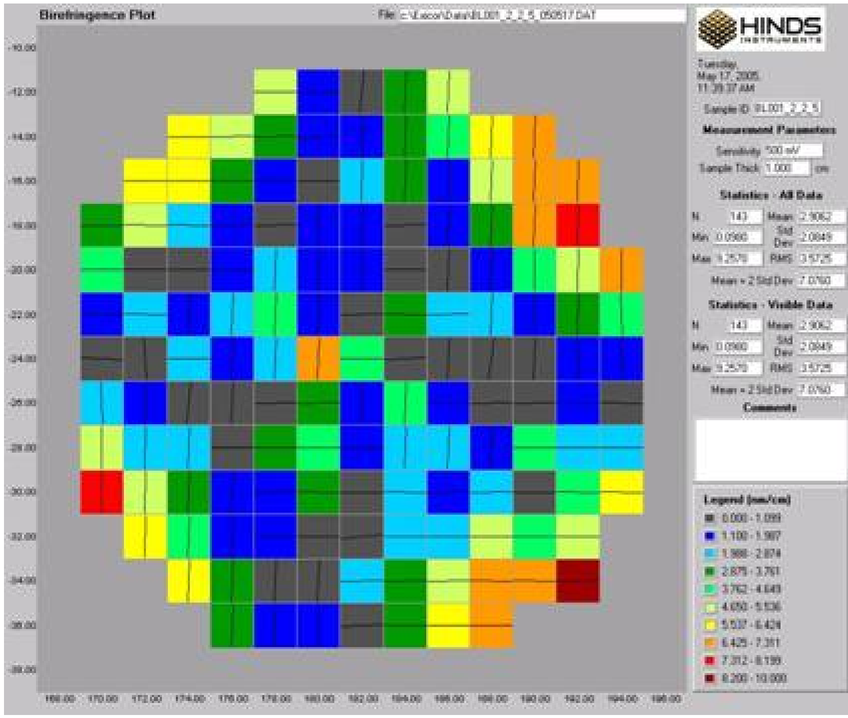
**$CaF_2$ by CZ**

**No sub-grain structure was observed**

**Possibility of good index homogeneity (Striae)**

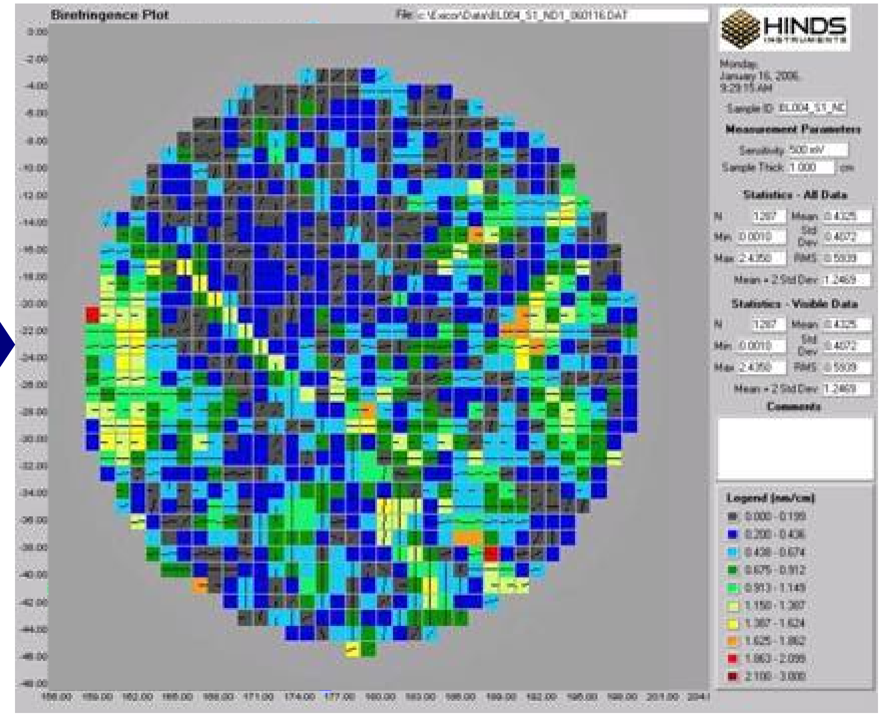
# SBR@633nm of $BaLiF_3$

## Before Annealing




RMS=3.57nm/cm
MAX=9.26nm/cm

## After Annealing




RMS: 0.63nm/cm
MAX:1.97nm/cm

Further Improvement would be possible