Lentilles GRIN (Gradient Refractive Index) transparentes dans l'infrarouge

Roscoff,
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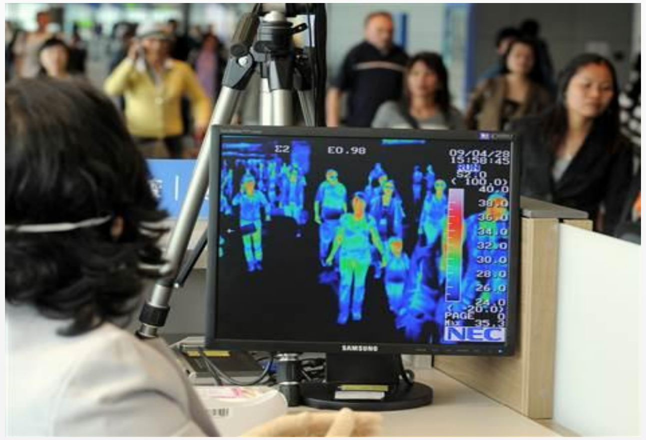
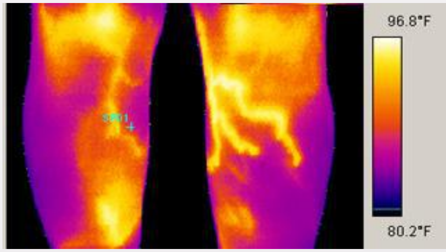
Context

Thermal imaging is still a growing market

…even more than expected



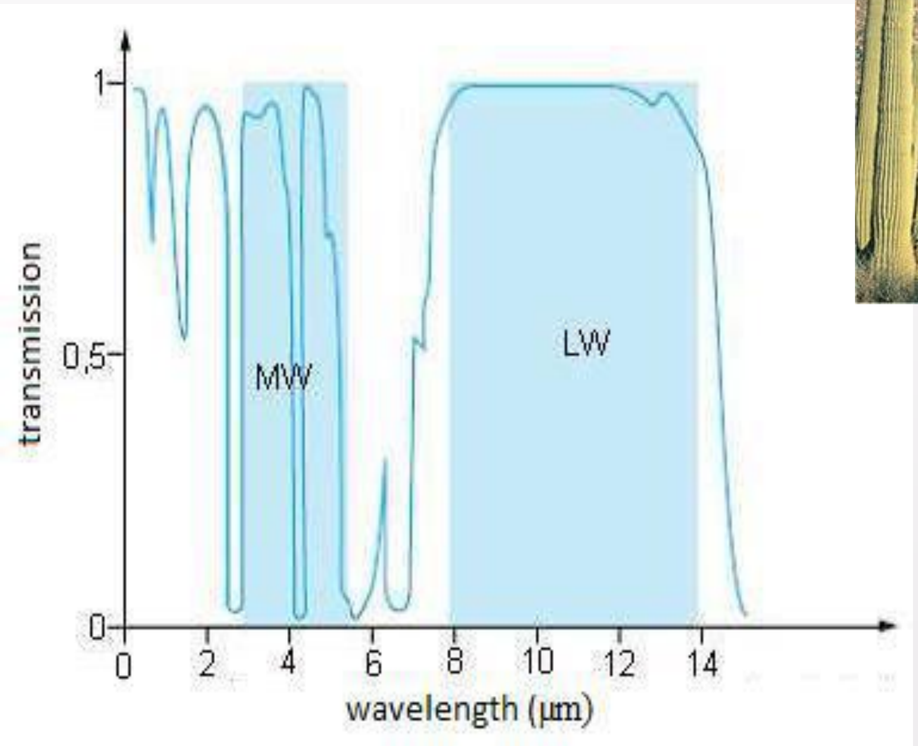


Progressive improvement and miniaturization of detectors, electronics and optics

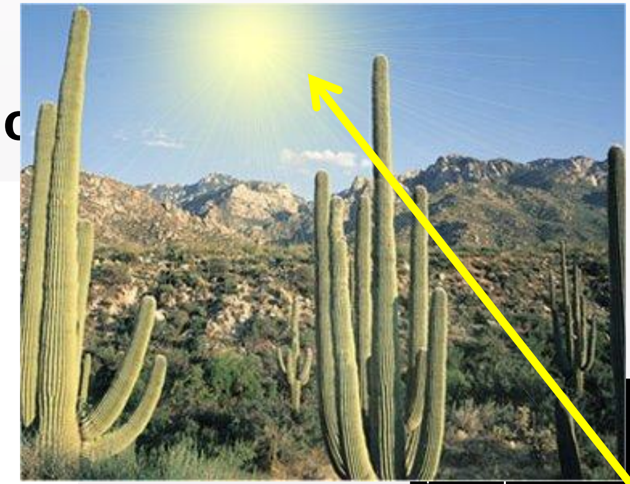
Need for cheaper, more efficient materials

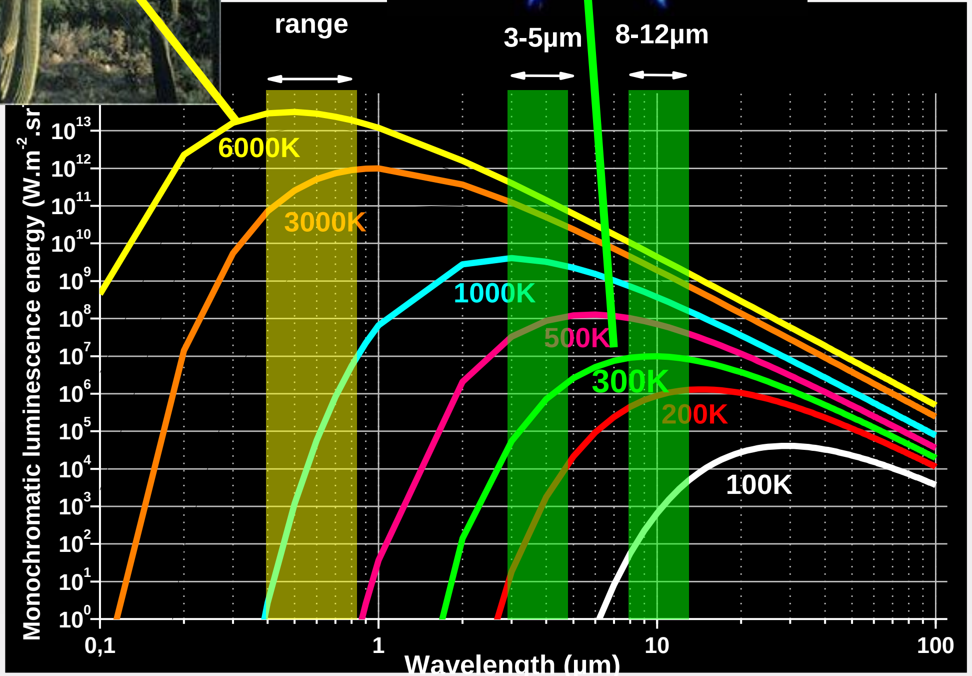
Thermal imaging

Based on the detection o… by hot



Atmospheric transmission





Needs for materials transparent in these IR bands

Single Crystalline Ge

- Expensive
- Needs diamond grinding


Polycrystalline ZnSe

- Synthesized by CVD
- Shaped by mechanical grinding

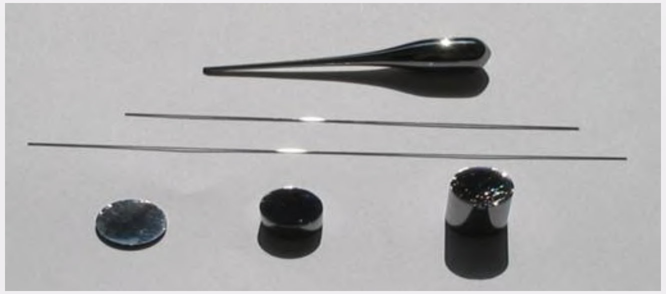
Chalcogenide glasses (Se)

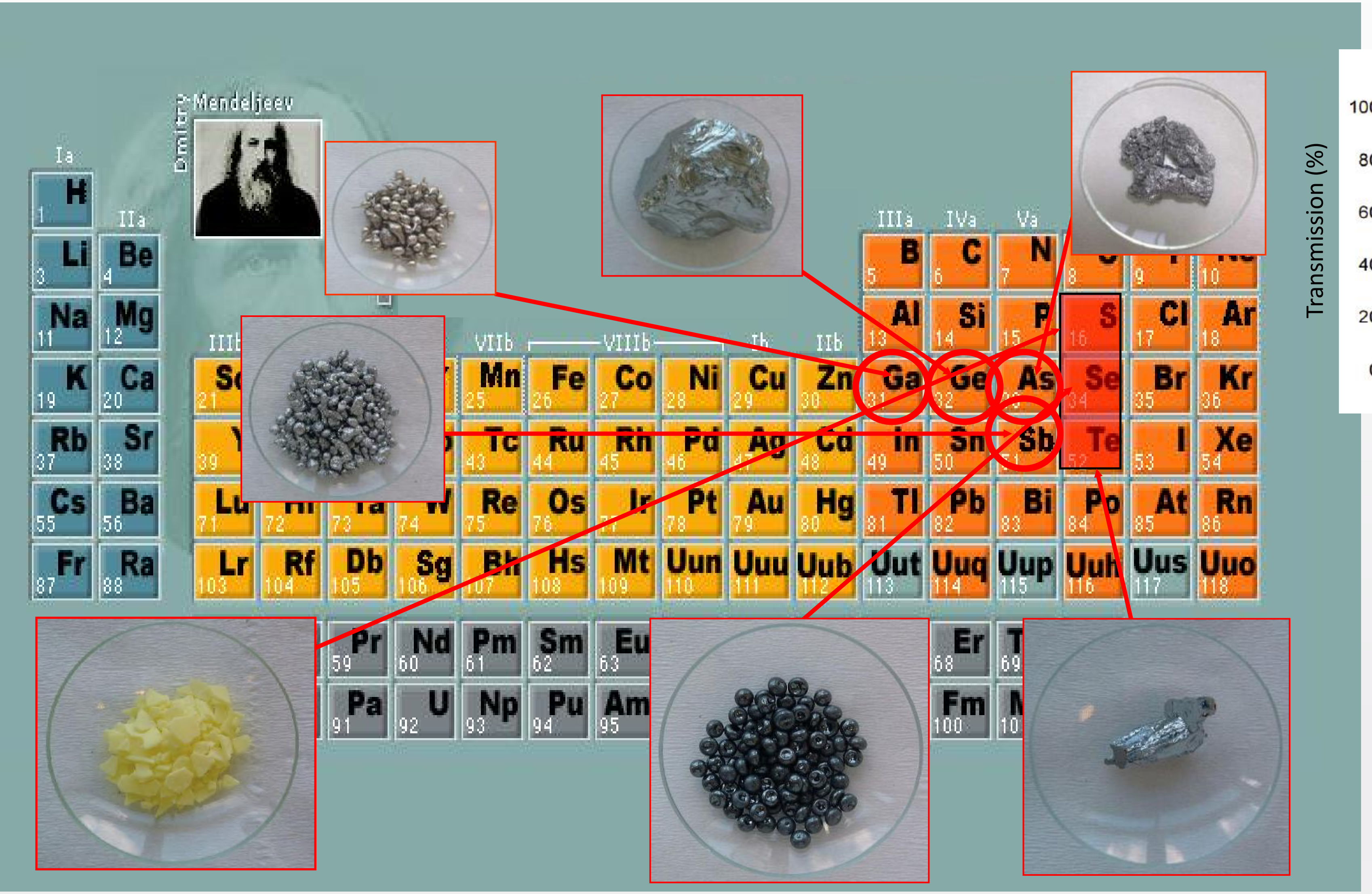
- Transparent from **800nm-16µm**
- **Cheaper**
- ***Shaping by molding at T>Tg (lenses, fibers..)***

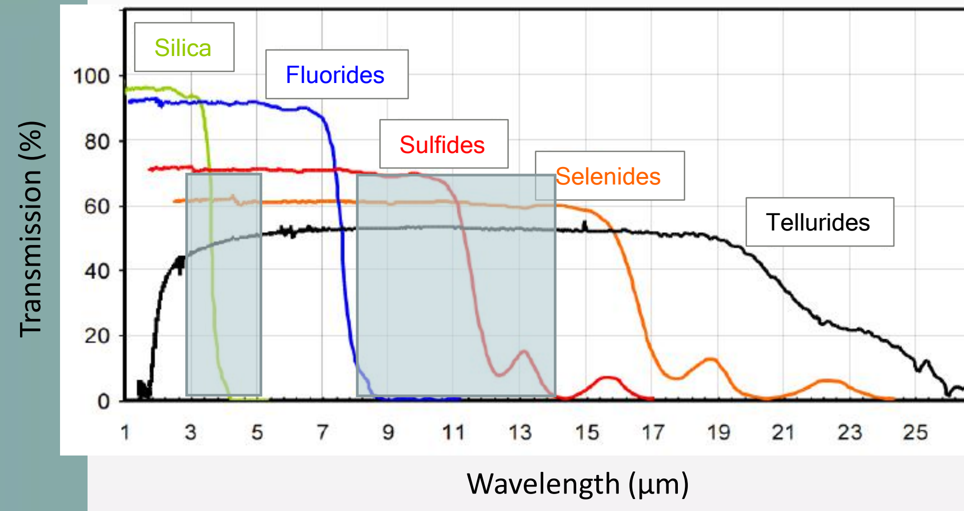
But

- **Synthesis in silica tubes**
- **Weaker mechanical properties**

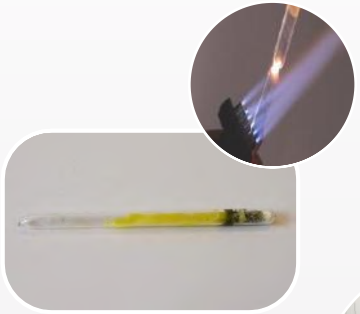
GASIR1® ($Ge_{22}As_{20}Se_{58}$) glass lenses, UMICORE





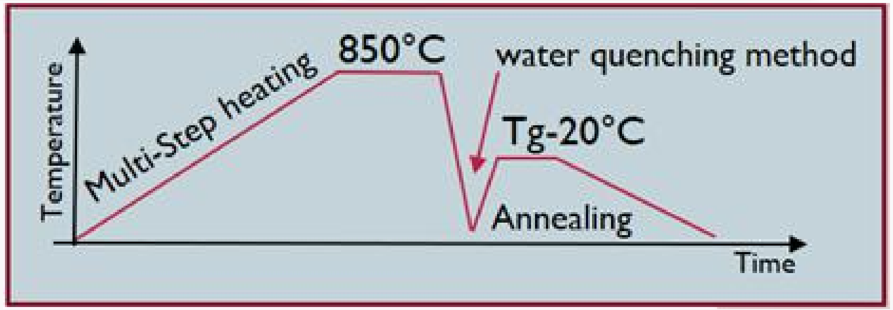


Work with Se glasses for being transparent in the LWIR (8-14µm)



Sealing under vacuum

High temperature melting



Thermal quenching

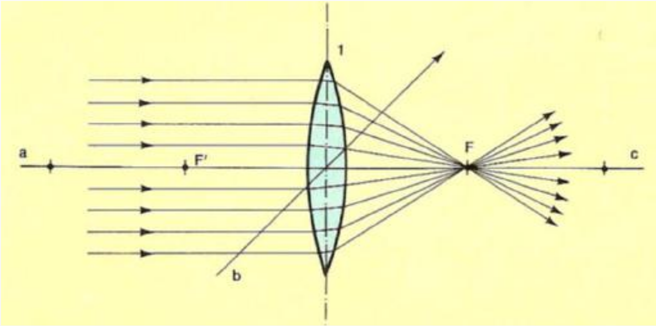
Glass synthesis
Melting-quenching technique

Alternative technique:
Mechanical milling/Flash sintering

Se - Glass

Classical Lenses

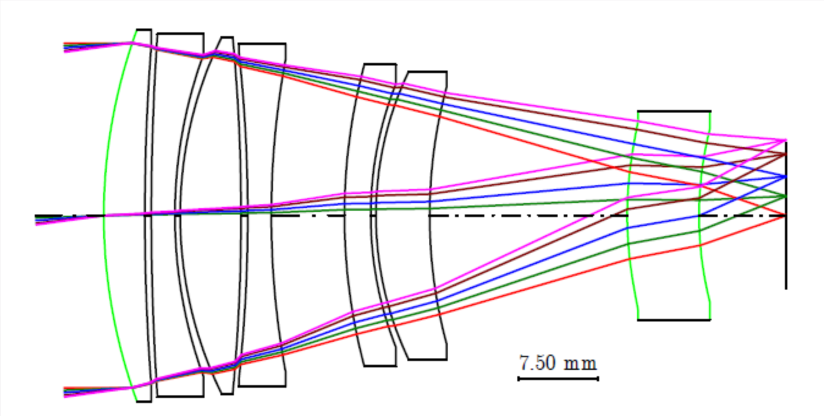
- Homogeneous refractive index
- Optical power is given by curved surfaces
- Combination of multiple lenses to obtain high-quality image



Main drawback : size of the optical system in case of compact equipment

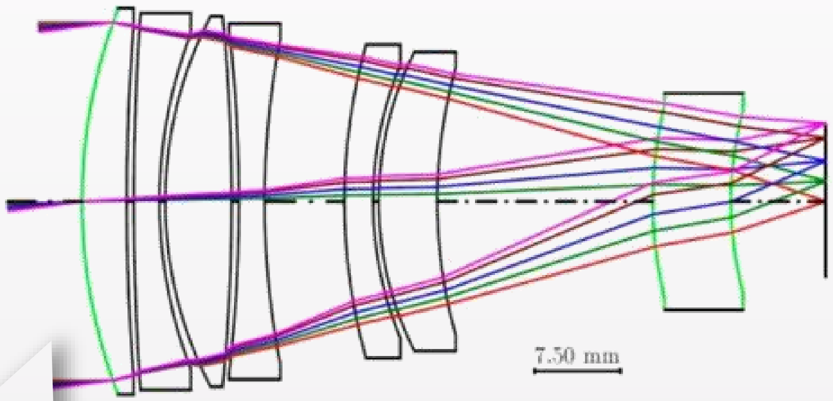
GASIR® Lenses

Optical device

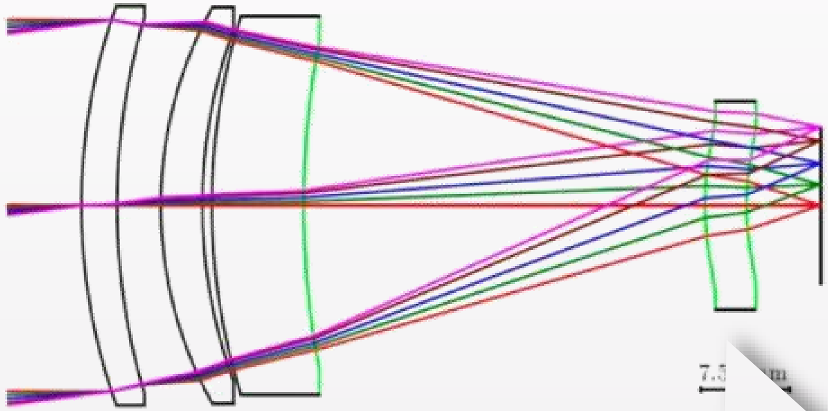


Conventional, homogeneous SWIR-LWIR optical design

Boyd, A. M. Optical design of athermal, multispectral, radial GRIN lenses. (International Society for Optics and Photonics, 2017).



*System composed of **homogeneous materials** and aspherical surfaces (green)*



*System composed of **GRIN** materials and aspherical surfaces (green)*

<u>OBJECTIVE</u>

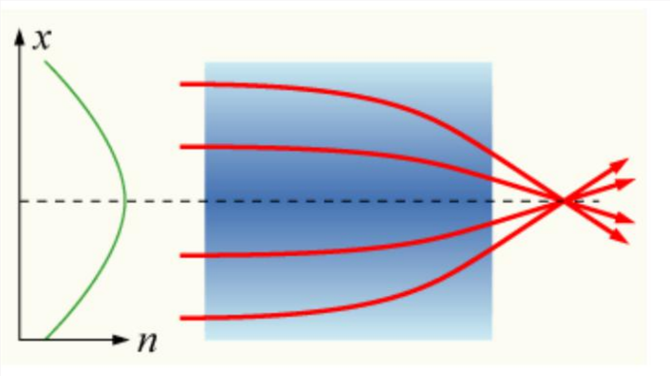
Reduction of the SWAP(***Size*** and ***Weight*** & ***Power***) for the IR optical systems

GRIN Lenses

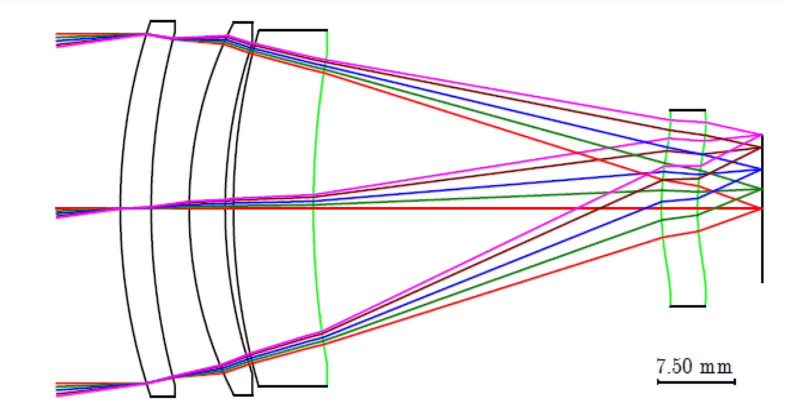
- Refractive index varies spatially
- Focus light by changing the refractive index of the lenses

Advantages :

- Giving more freedom for the optical design such as simple shape
- correct efficiently thermal and chromatic aberrations
- Reducing number of lenses in the optical device
- Lowering size, weight, and cost of the camera

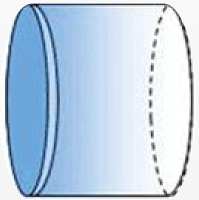


A flat GRIN lens focuses light by changing the refractive index

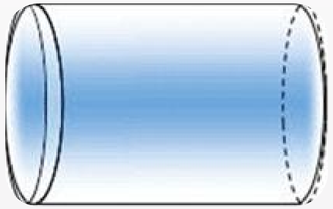


Multispectral GRIN lens optical design

2 main types of GRIN used in chalcogenide glasses:



Axial Gradient



Radial Gradient

Several manufacturing techniques :

- Thermal poling *[Lepicard, A. et al. Long-lived monolithic micro-optics for multispectral GRIN applications. Sci. Rep. 8, 7388 (2018)]*
- Laser irradiation *[Kang, M. et al. Refractive index patterning of infrared glass ceramics through laser-induced vitrification. Opt. Mater. Express 8, 2722-2733 (2018)]*
- Inter-diffusion between different layers of glasses *[Gibson, D. et al. IR GRIN optics: design and fabrication. in Advanced Optics for Defense Applications: UV through LWIR II 10181, 101810B, 2017)]*

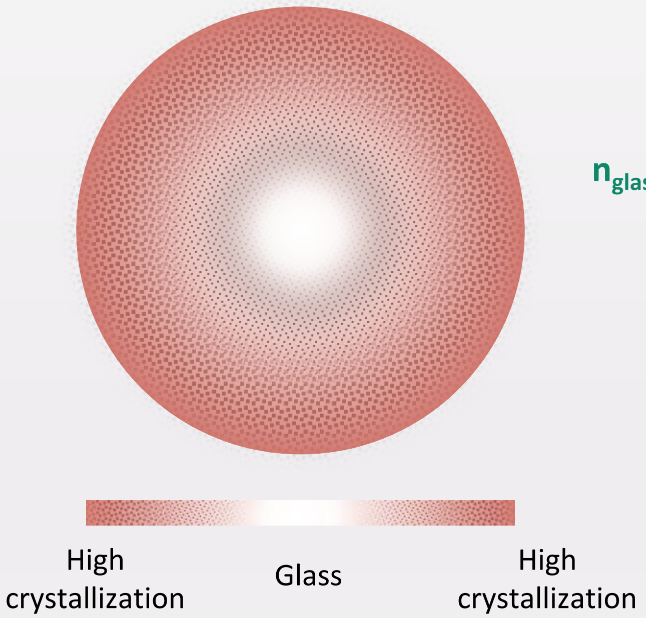
Our methods to develop radial GRIN:

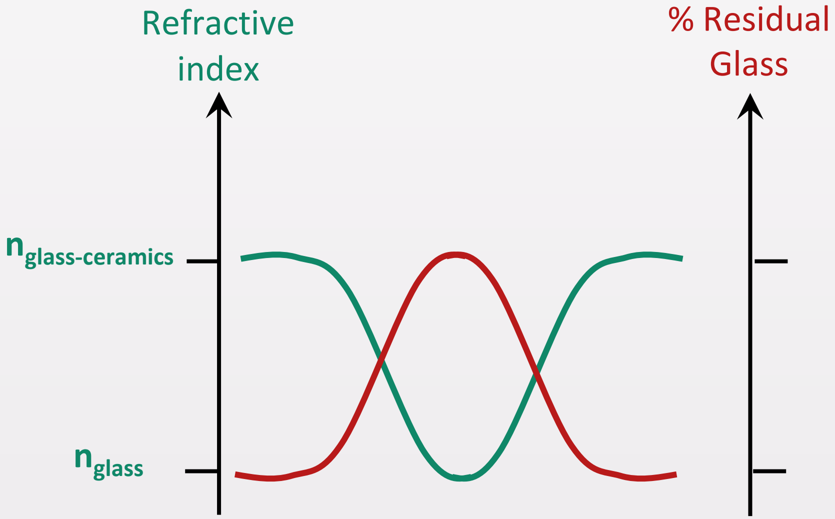
- 1/ Controlled crystallization
- 2/ Ionic exchange

Why controlled crystallization ?

Crystals created in the glass can induce a variation of the refractive index

Create a bulk glass-ceramics where the two states coexist :
- Glassy matrix
- Crystals



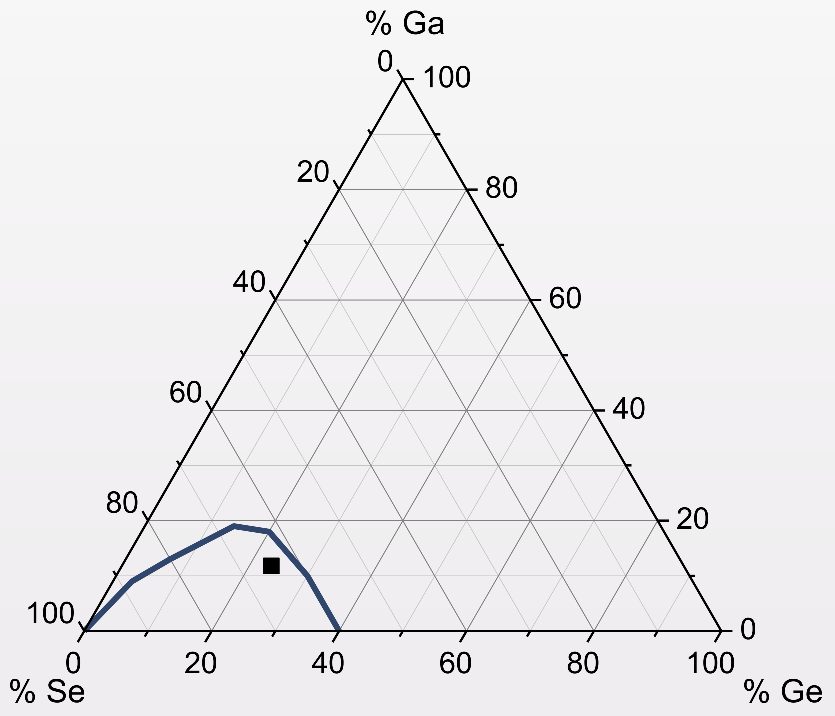


First approach:

Determination of the variation of refractive index during crystallization

Study of the ternary system : Ge - Ga - Se

➢ 80 $GeSe_2$ - 20 Ga_2Se_3



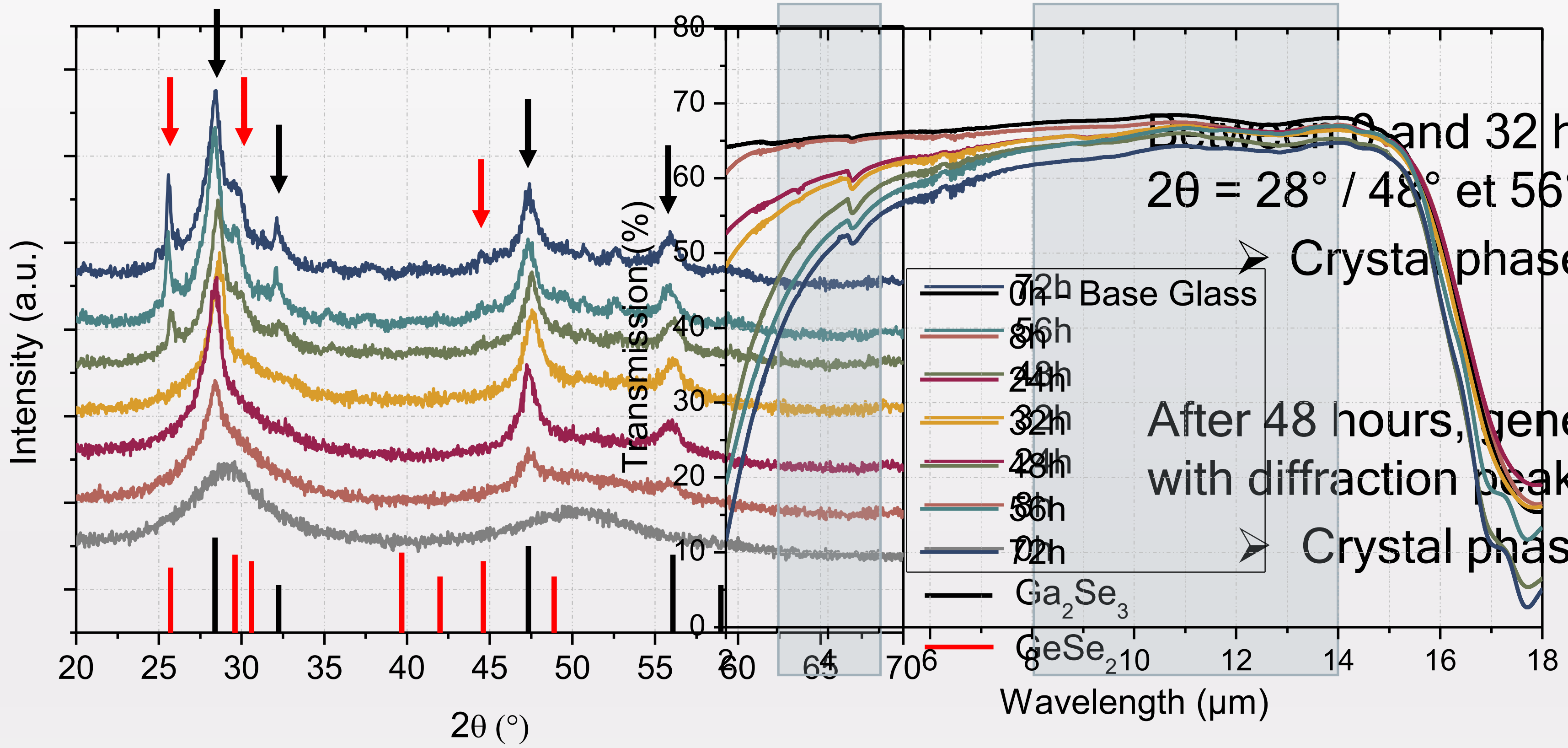
Method used for controlled crystallization:

1. Synthesis of the glass by melt/quenching method
2. Crystallization in ventilated furnace at T > T_g (usually Tg+30°C)

L. Calvez, Comptes Rendus Physique, 18, 2017

Annealing time
@ Tg+30°C : 380°C

- Good IR transmission (MWIR and LWIR) until 48 hours
- 2 crystals phases are generated and observed by XRD



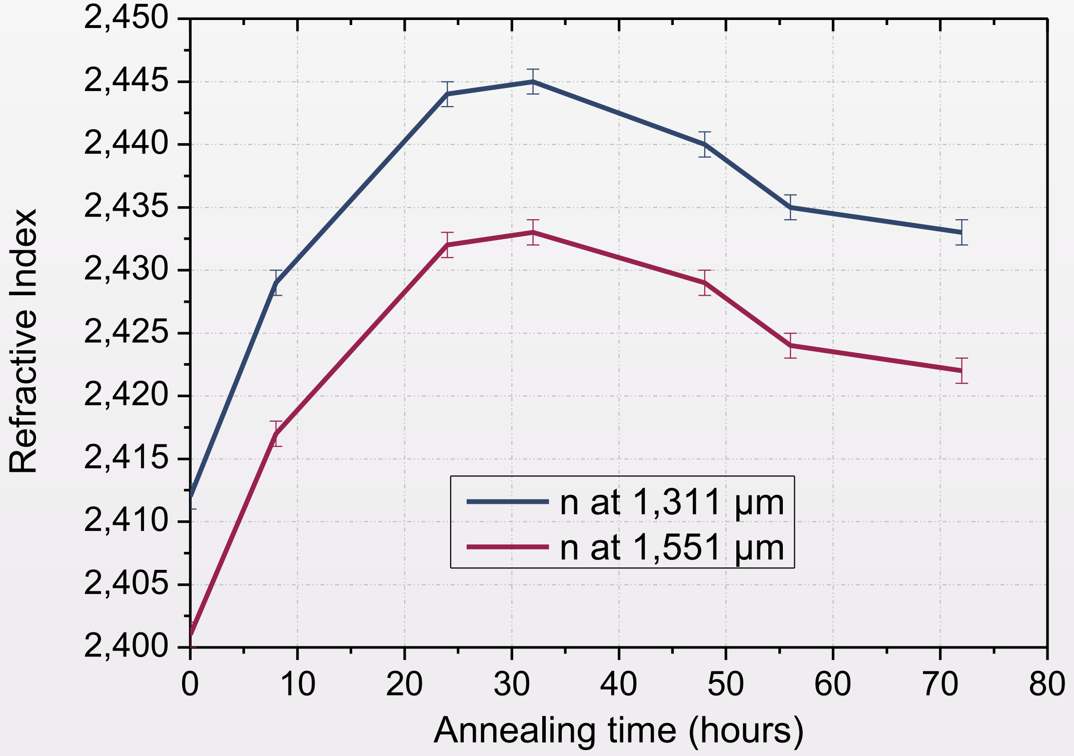
Between 0 and 32 hours, diffraction peaks at 2θ = 28° / 48° et 56°

➢ Crystal phase Ga_2Se_3

After 48 hours, generation of new crystal phase with diffraction peaks at 2θ = 15, 25° et 32 °

➢ Crystal phase $GeSe_2$

Generation of crystals within the glassy matrix → Variation of the refractive index measured by Metricon (M-line technique) @ 1.311 and 1.551 µm

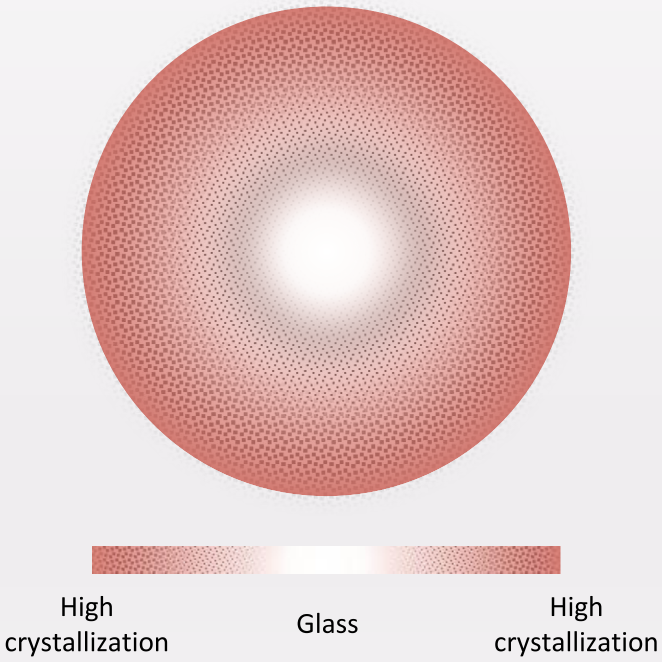


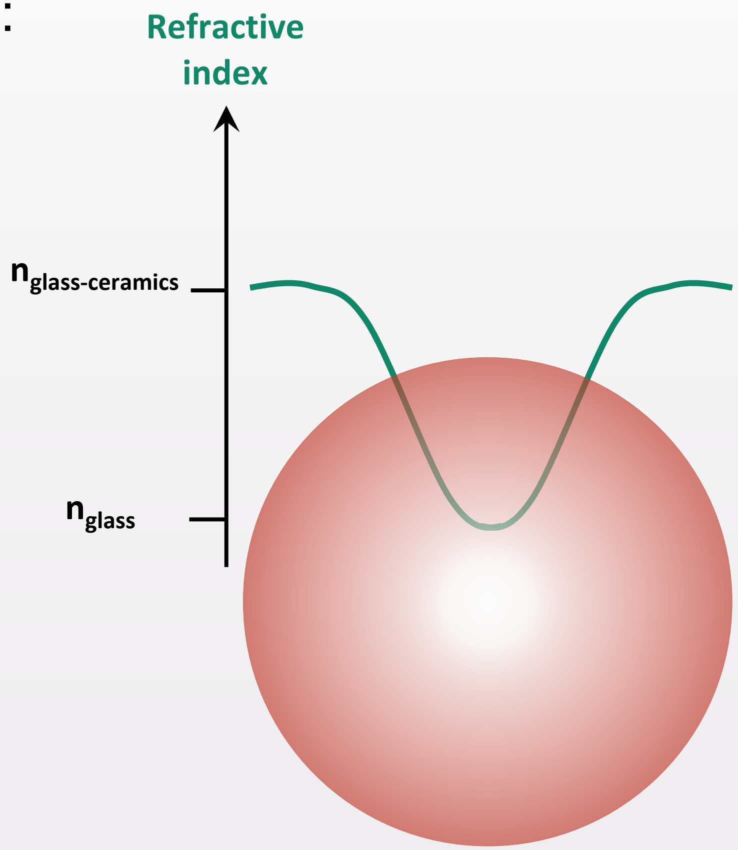
- Significant **variation of the refractive index (+ 0.032)** between the base glass and glass-ceramics 32h
  - ➢ Corresponding to **Ga_2Se_3 phase**
- Then, decrease of the index after 48h of annealing
  - ➢ Generation of **$GeSe_2$ phase**

Challenges to tackle

Create a **heterogeneous bulk glass-ceramics** with:

- Nanoparticles (for transparency)
- Highest rate of crystals on the edge
- Still amorphous in the center





How to induce a gradient of crystallization ?

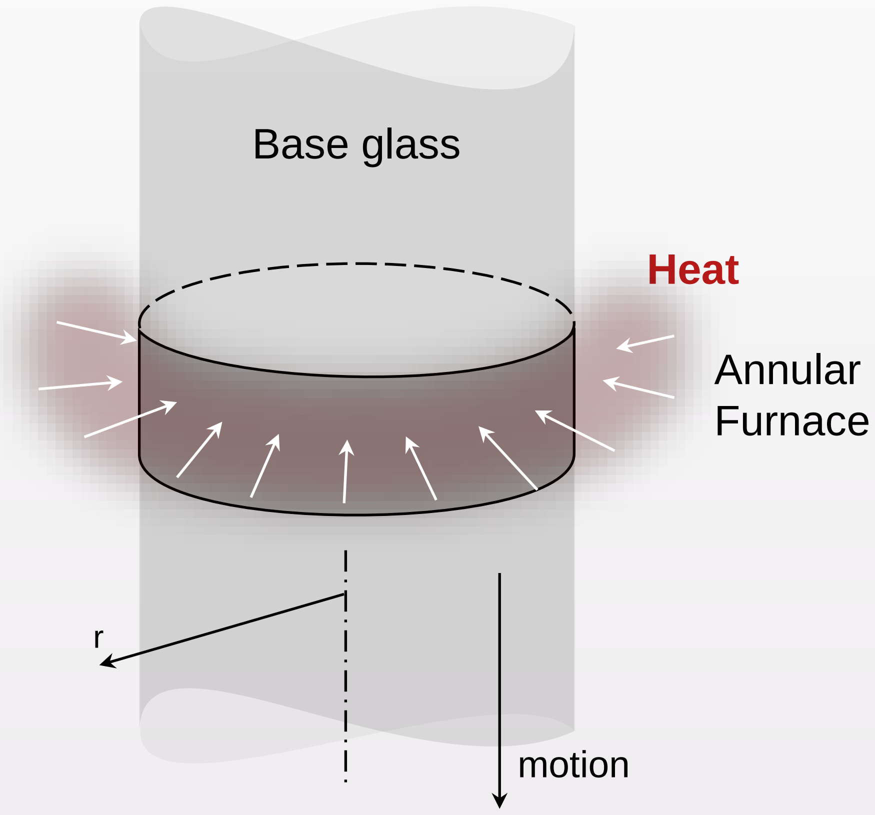
➡ Use of a tower to draw fibers!

Annular furnace : Small heating zone
Inhomogeneity of the temperature

Create a gradient of crystallization

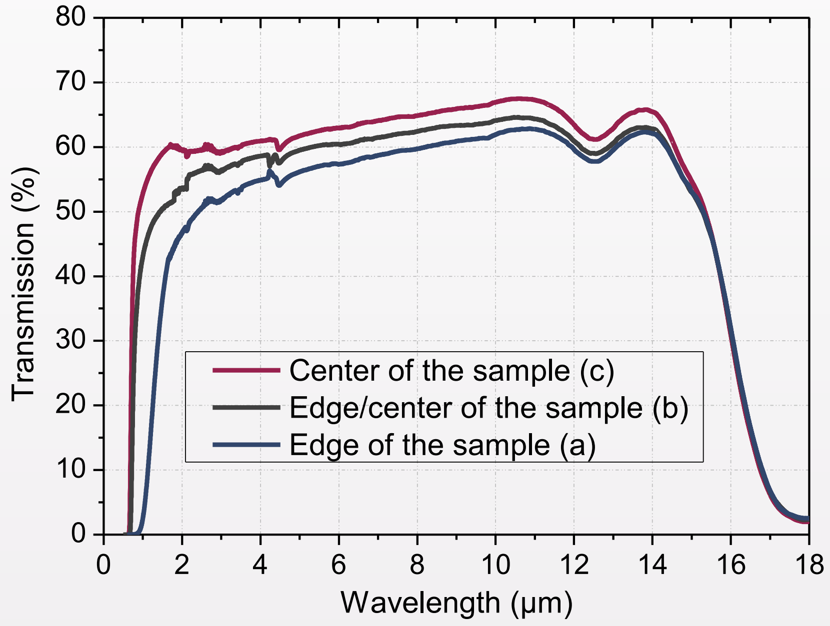
⬇

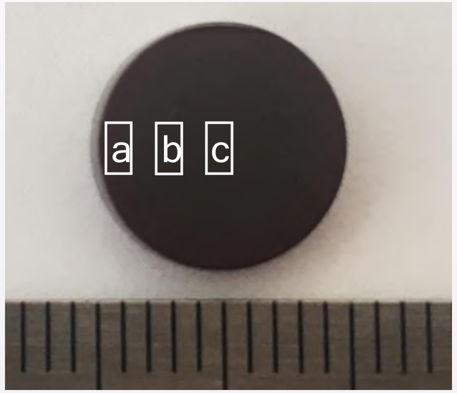
Create a Gradient of Refractive INdex

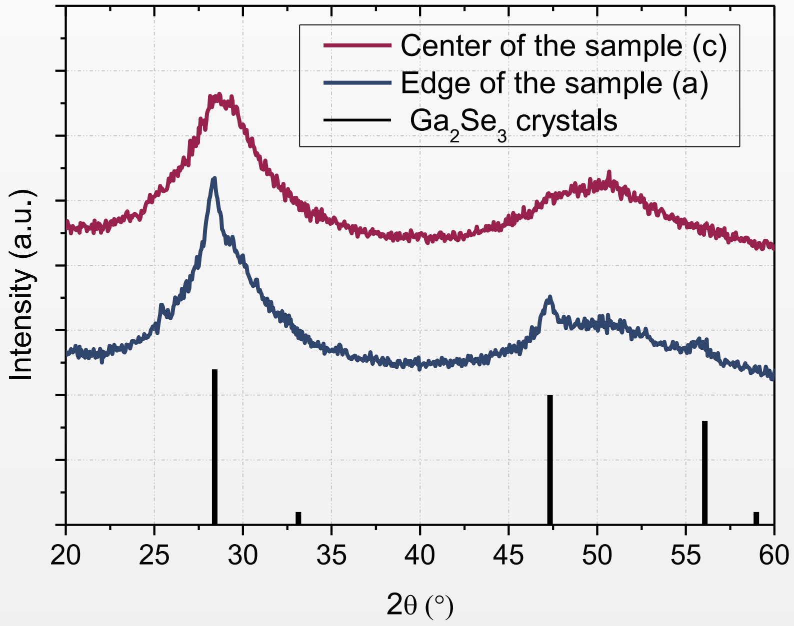


➡ Need to control several parameters : temperature, motion of the bulk, He flow

Use of glass rods of 8cm long and 10mm diameter



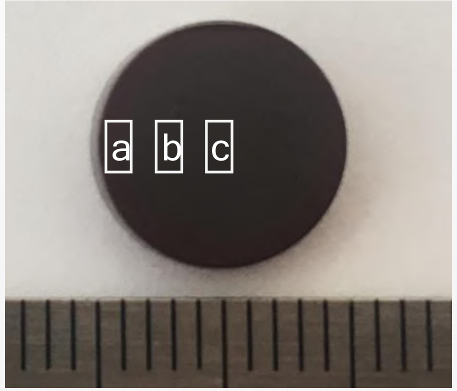




- Rayleigh scatterings attesting presence of crystals
- Crystals slightly affect LWIR transparency

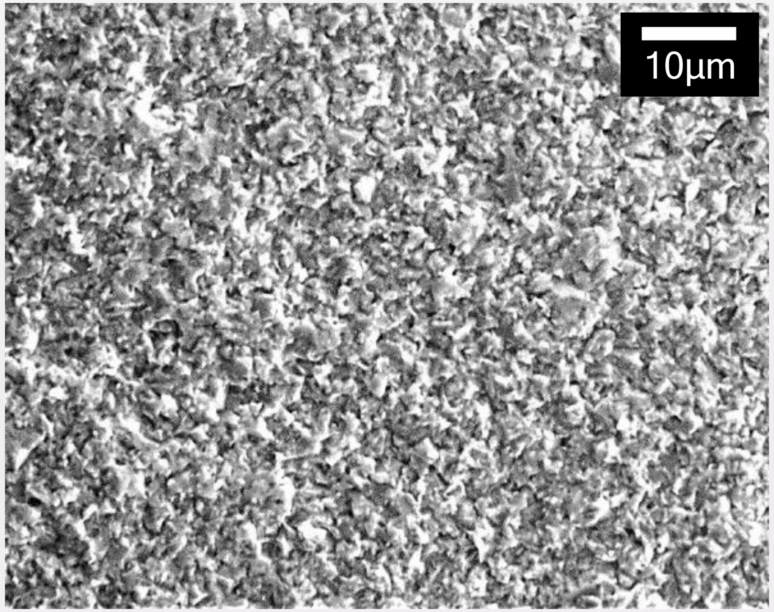
- Difference between edge and border of the sample
- Peaks associated to Ga_2Se_3 crystals phase

SEM Images performed at different place in glass-ceramics

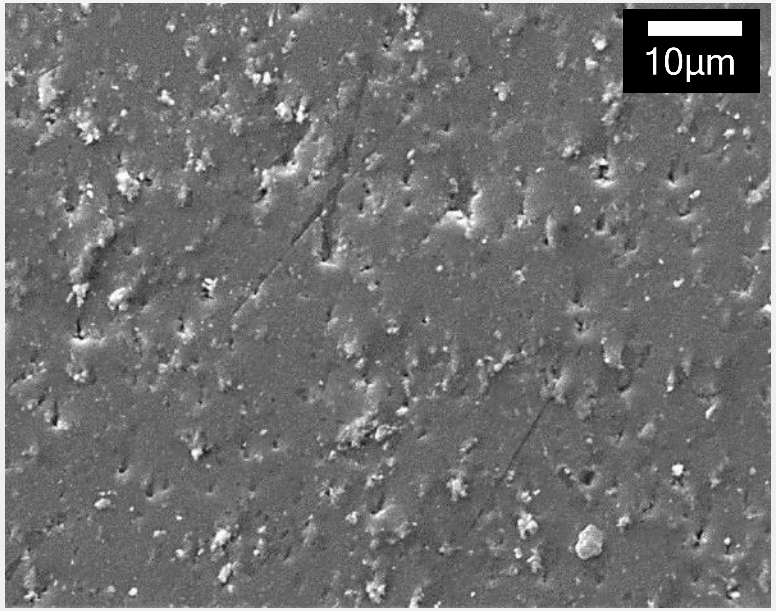


- Density and crystals size decrease progressively
- Homogenous and high degree of crystallization
- Until having amorphous structure in sample center
= Size Ga_2Se_3 crystals about 250 nm

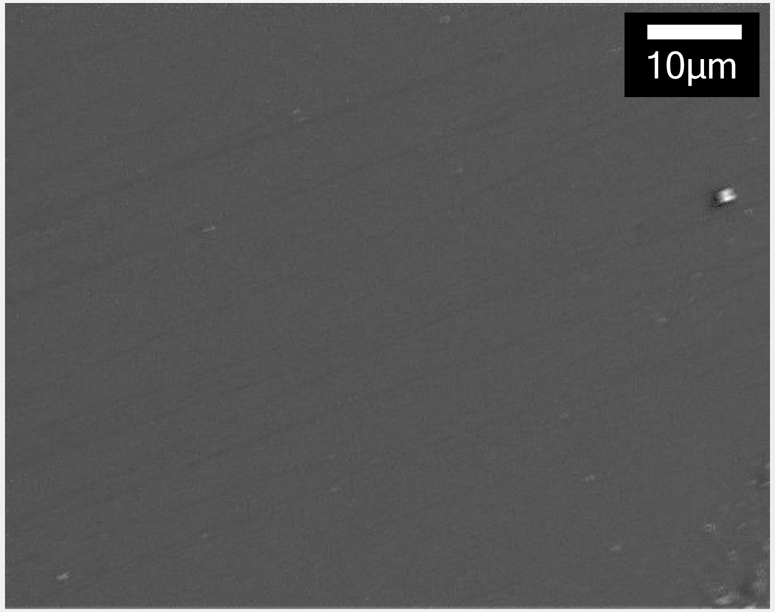
a.



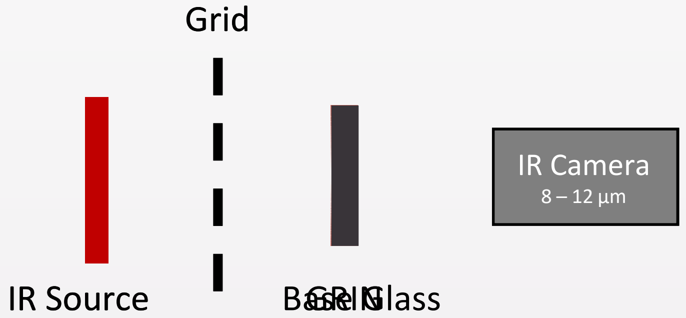
b.

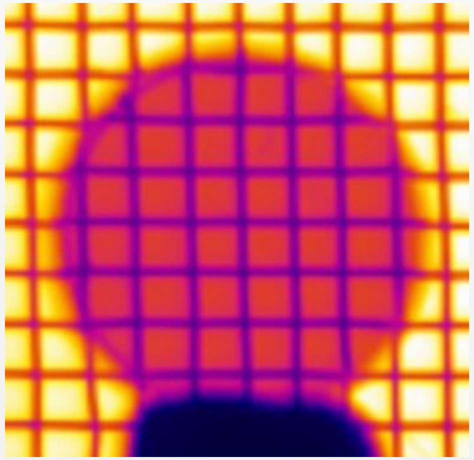


c.

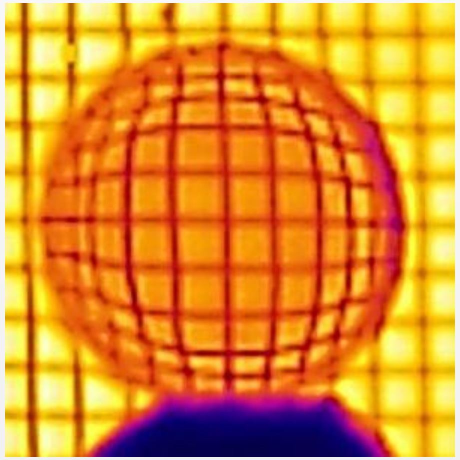


Observation through IR camera





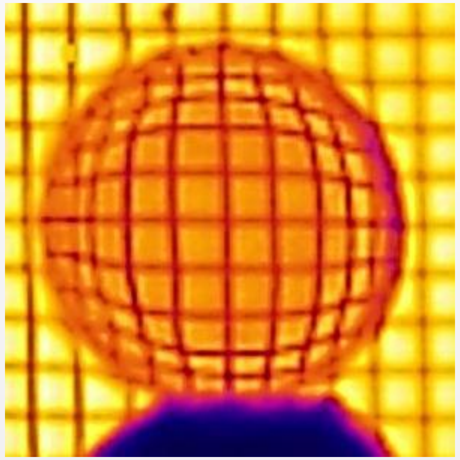
Base glass



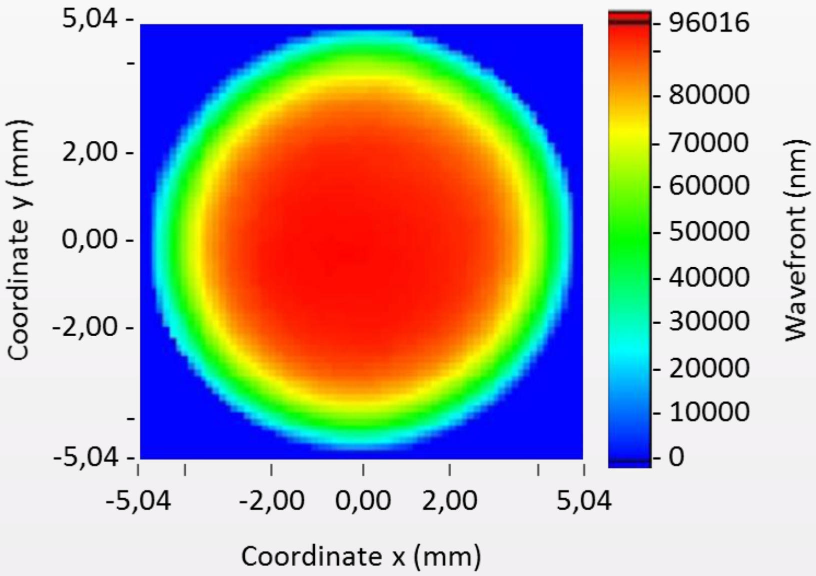
Glass-ceramic with Radial GRIN

- **Deformation of the grid image** placed behind glass-ceramic with radial crystallization
- Highlighting **Gradient Refractive Index** induced by creation of crystals in base glass

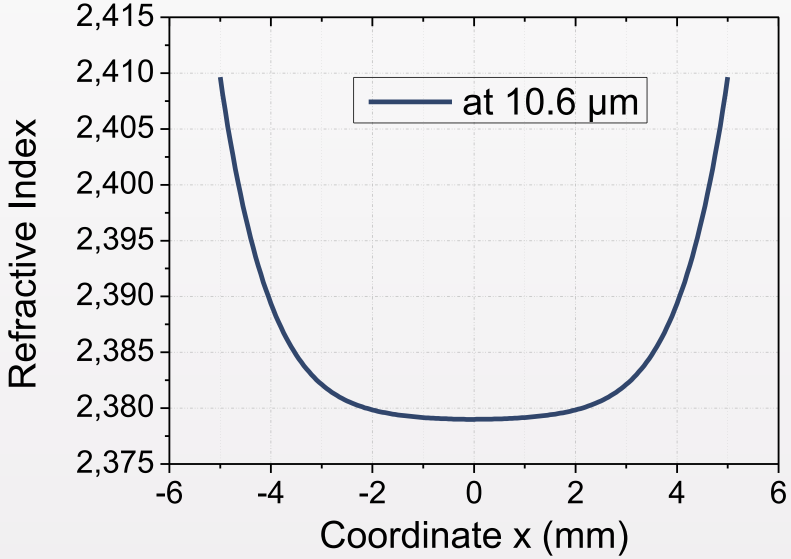
Measure Δn of the GRIN through Wavefront analyzer at 10.6 µm



Radial GRIN



Wavefront delay



Profil Index calculated

$\Delta n_{measure} = 0.03 \pm 2.10^{-3}$

Corresponding to bulk crystallization :
Δn = 0,032

Difficulty to perfectly reproduce the process

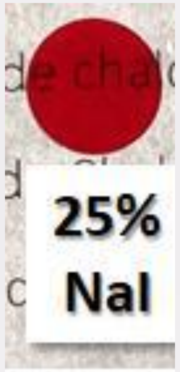
E. Lavanant, Optical Materials Express Vol. 10 (4), 2020

GRIN lenses prepared by ionic exchange in chalcohalide glasses

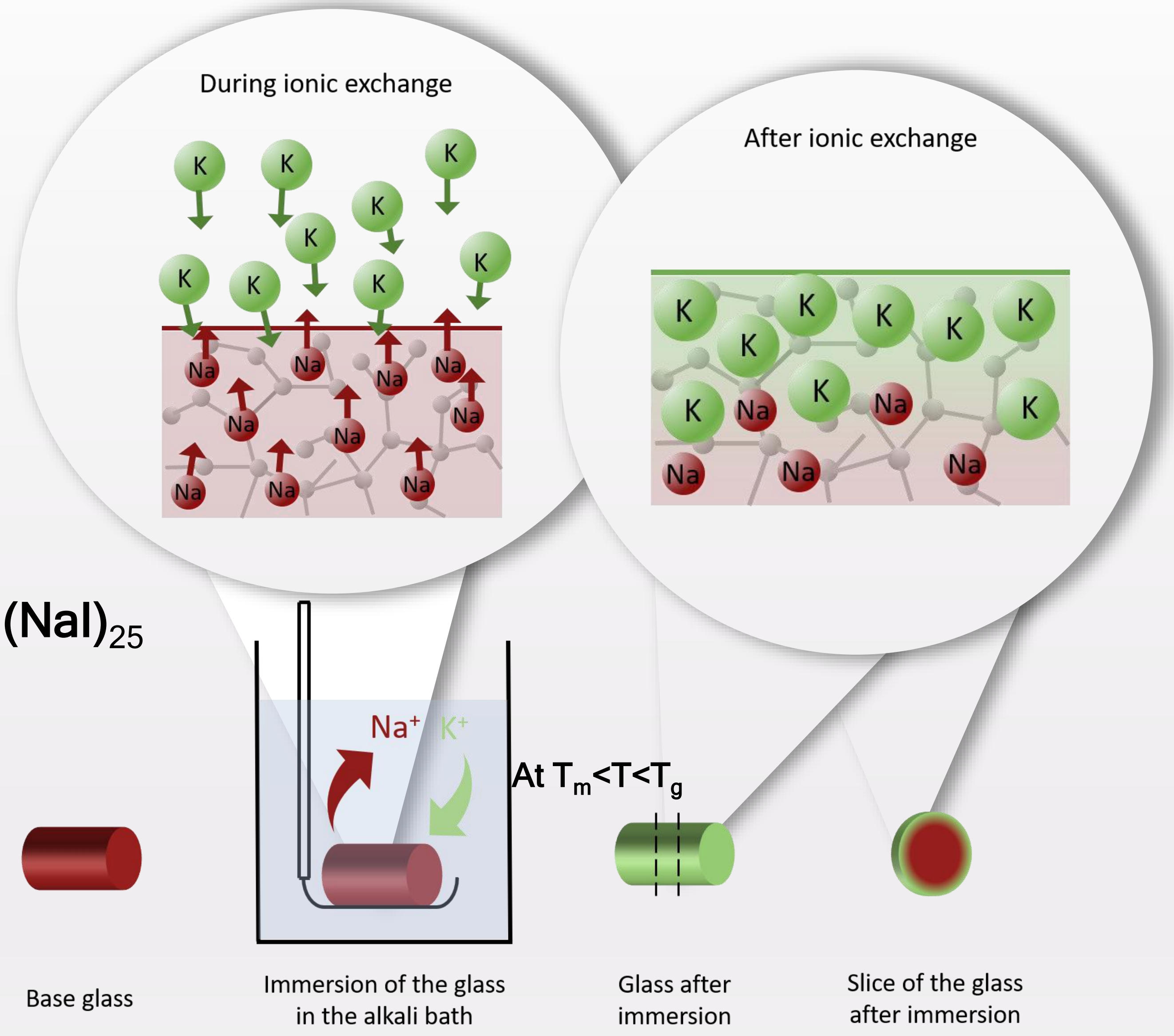
THE GLASS

- ✓ High T_g
- ✓ High rate of **alkaline**
- ✓ 8-12 µm : transparent

$(72\ GeSe_2 - 28\ Ga_2Se_3)_{75}\ \mathbf{(NaI)}_{25}$



$T_g = 300°C$



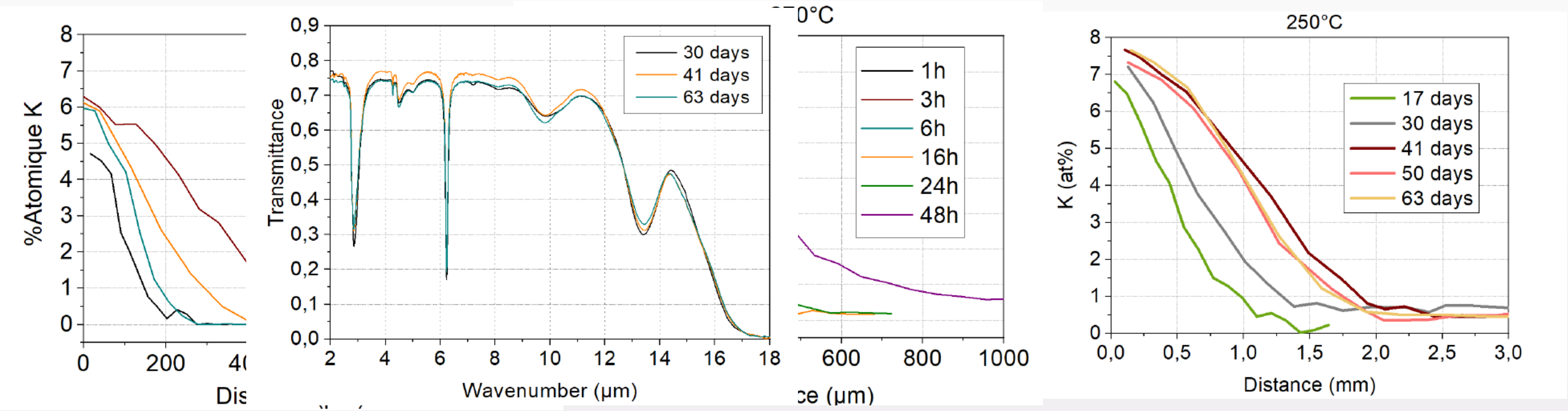
THE BATH

- ✓ Lowest Tm possible
- ✓ Highest rate of alkaline

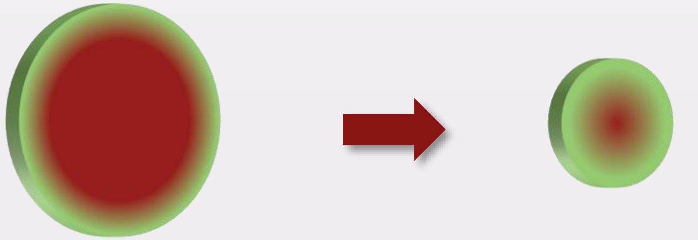
$60\ \mathbf{K}NO_3 / 40\ NaNO_3$

$T_m = 240°C$

DIFFUSION PROFIL of K^+ INSIDE THE GLASS (EDS)

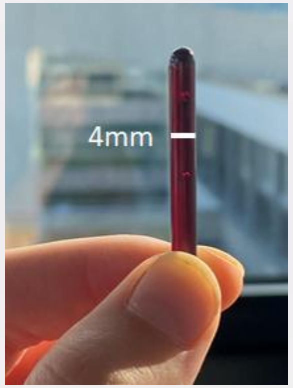


- Limitation due to NaI crystallization
- No pollution by O from nitrate bath
- ***2mm*** of diffusion reached for **40 days at 250°C**



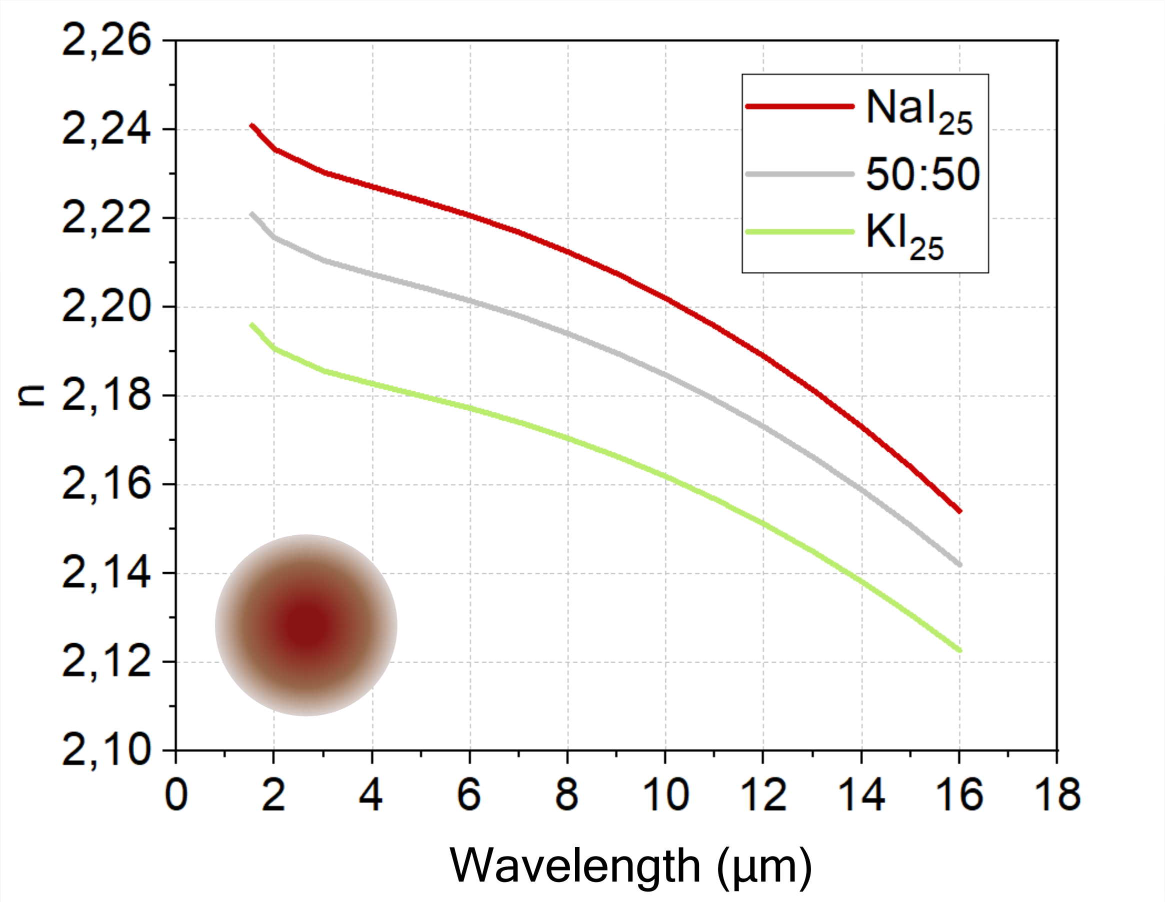
10mm sample

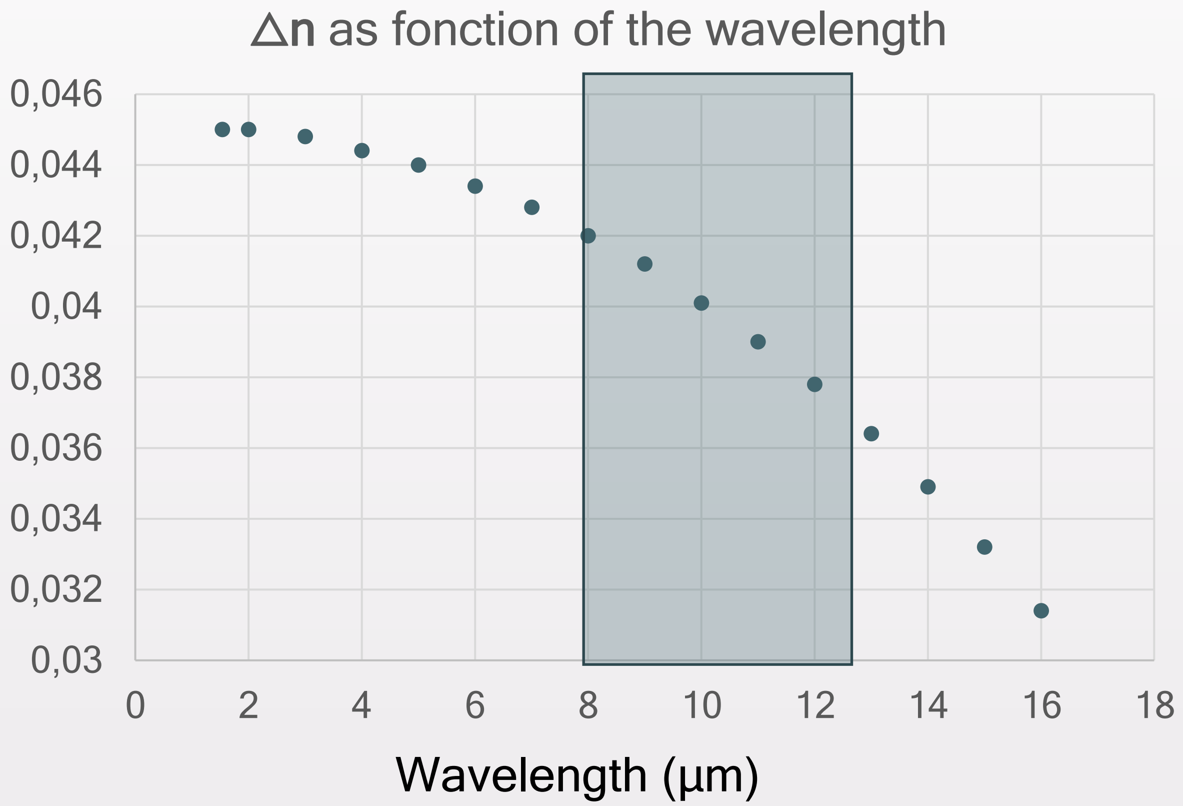
4mm sample



Δn AS FUNCTION OF THE WAVELENGTH

Measure on the base glasses

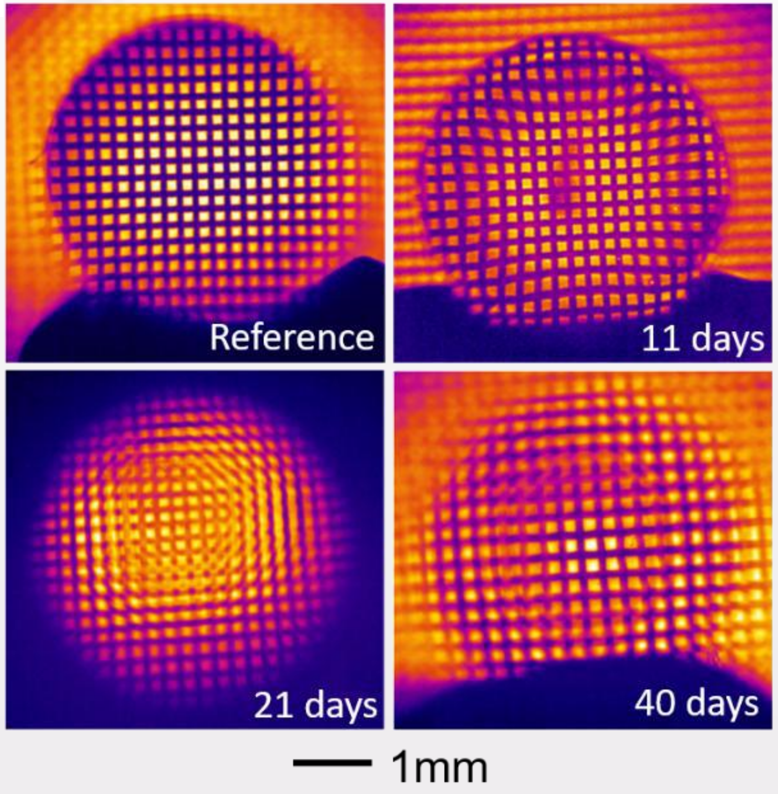




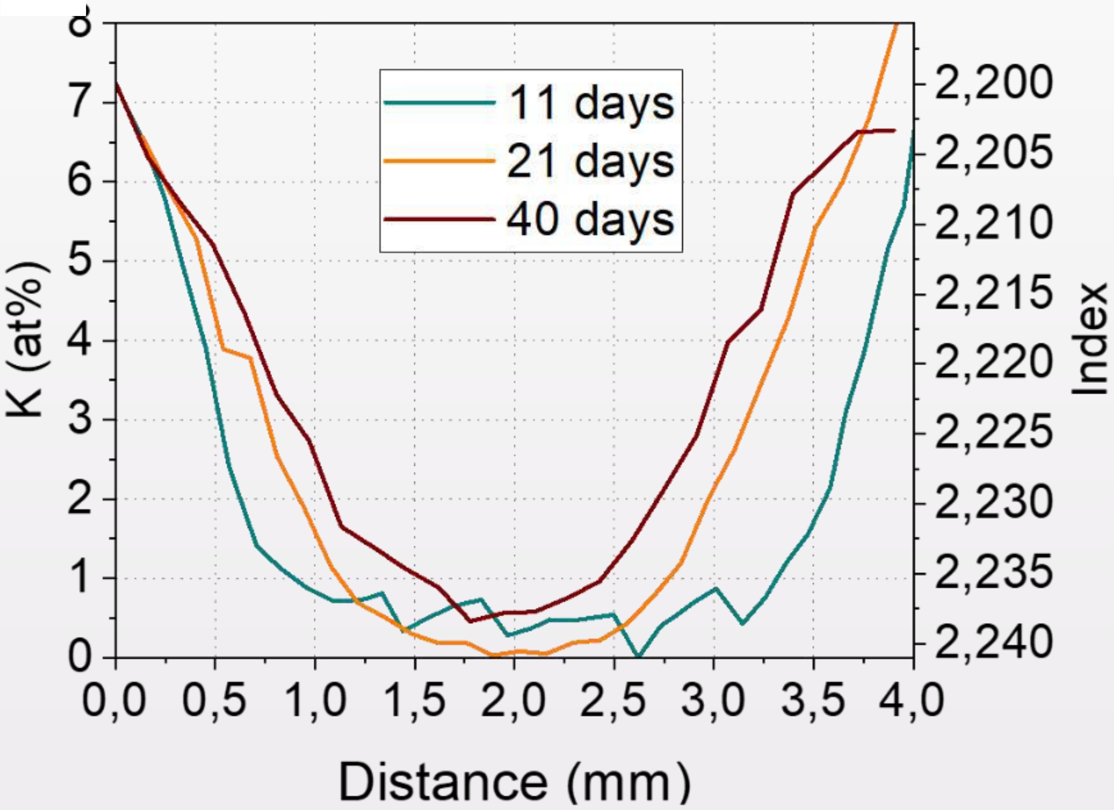
Expected Δn of 4.10^{-2} @8-12µm

IR GRIN LENSES OBTAINED BY IONIC EXCHANGE

Infrared camera observation



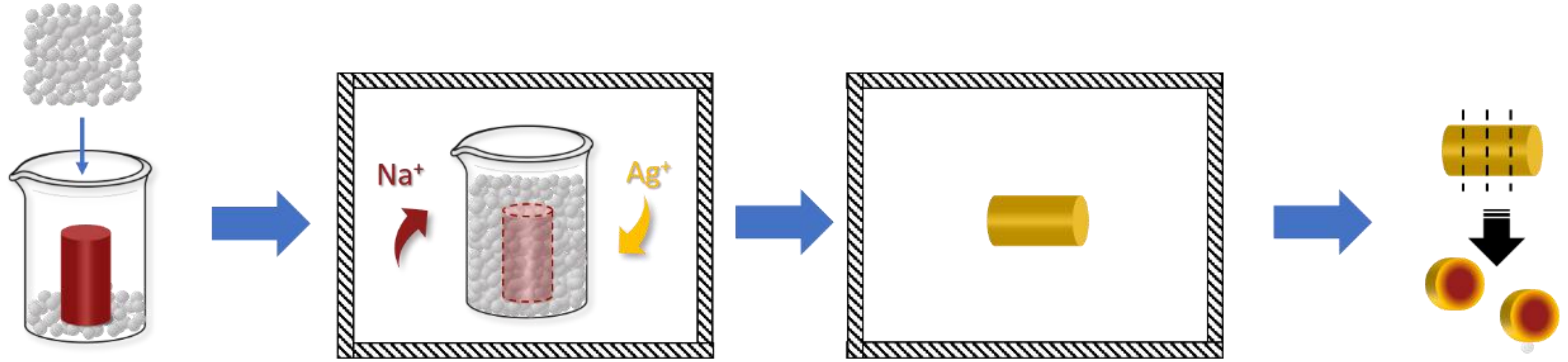
Diffusion and index profil



- Refractive index gradient is coherent with the diffusion profil
- **Δn max of - 4,5.10^{-2} , convergent** profile

C. Foumentin et al, Scientific Reports, vol.11, 2021

Ag^{+} ION EXCHANGE : a two step 'solid-solid' process

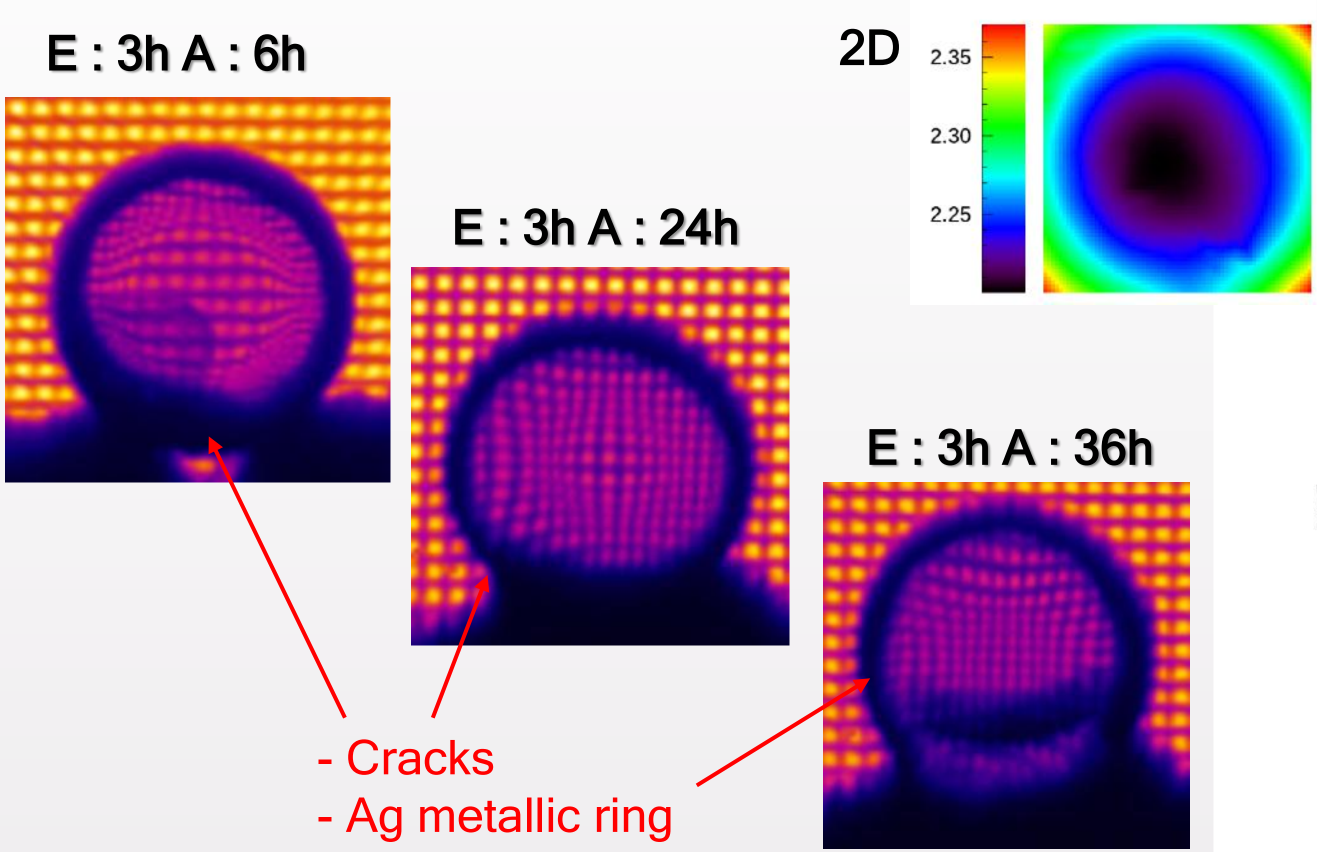


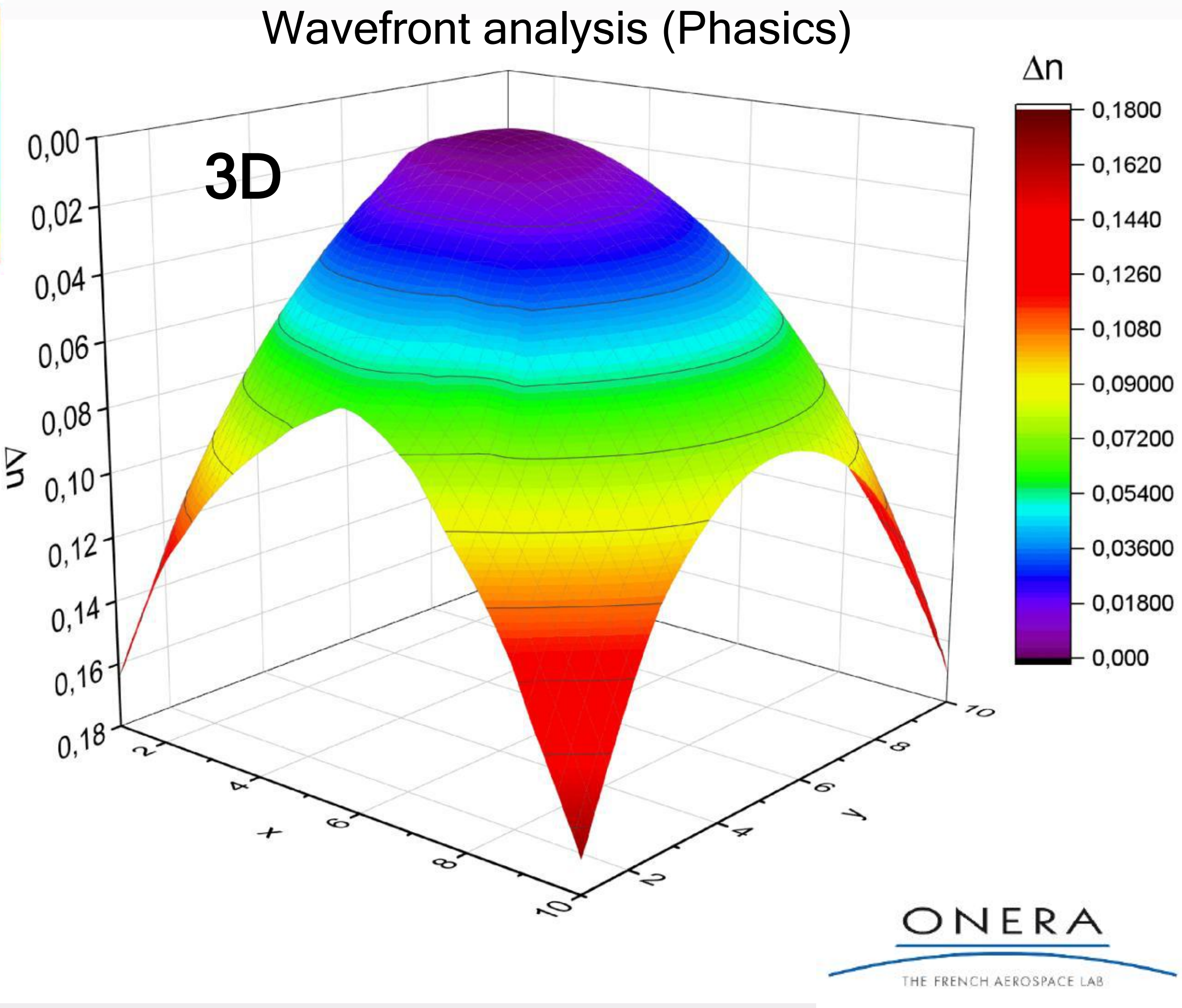
Glass rod **recovered by nitrates powder** → Thermal treatment for Exchange @ $T<T_{nitrates}$ → Annealing @ T=Tg → Radial GRIN lens obtained after cutting

COMPOSITION $(0{,}72GeSe_2 - 0{,}28Ga_2Se_3)_{75}\ (NaI)_{25}$

NITRATES $80\ KNO_3\ 20\ AgNO_3$

TEMPERATURE E : 250°C
A : 310°C

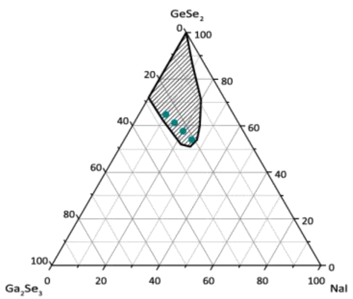


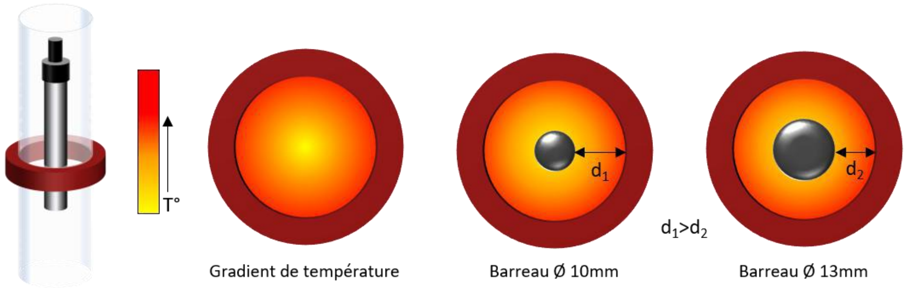


- Δn max measured = **1,8.10^{-1}**
- Polynomial profil of gradient
- Glass presents cracks on the edges

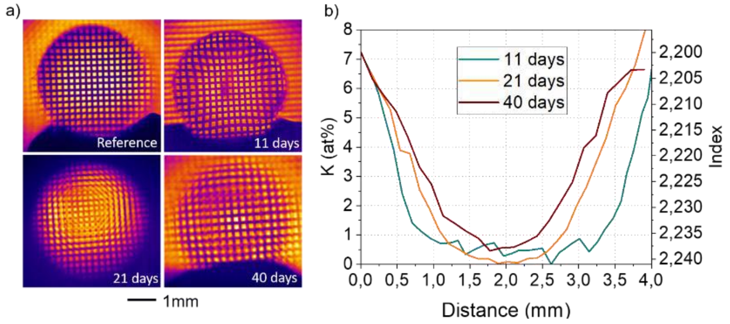
C. Fourmentin et al., Adv. Funct. Mater., 2312275, 2024

- Development of **controlled crystallisation** process
- Influence of cristallisation on **Δn**
- GRIN lens with **Δn** up to 4.10^{-2}

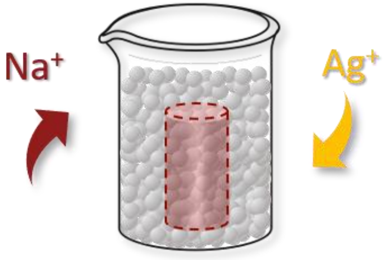


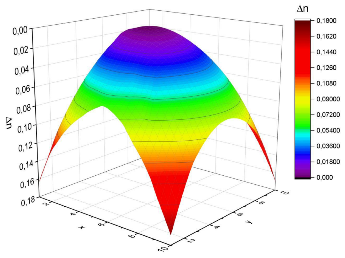


- Ionic exchange process **Na⁺/K⁺**
- Maximum diffusion depth : **2 mm (40 days)**
- **Convergente** GRIN lens of **4 mm** diameter with **Δn = 4,5.10^{-2}**



- Ionic exchange process **Ag⁺/Na⁺**
- Divergente GRIN lenses with **Δn** up to **1.10^{-1}**





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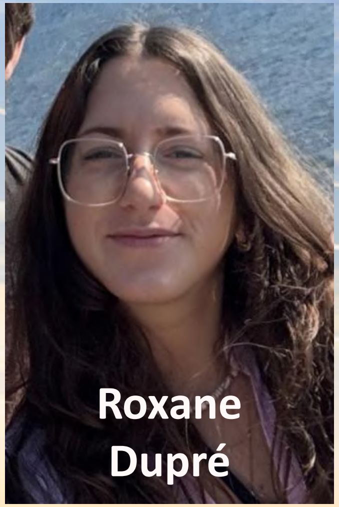
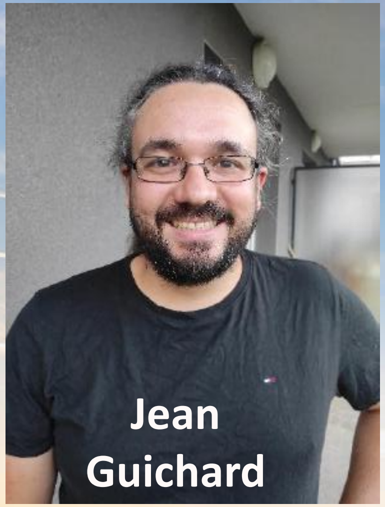


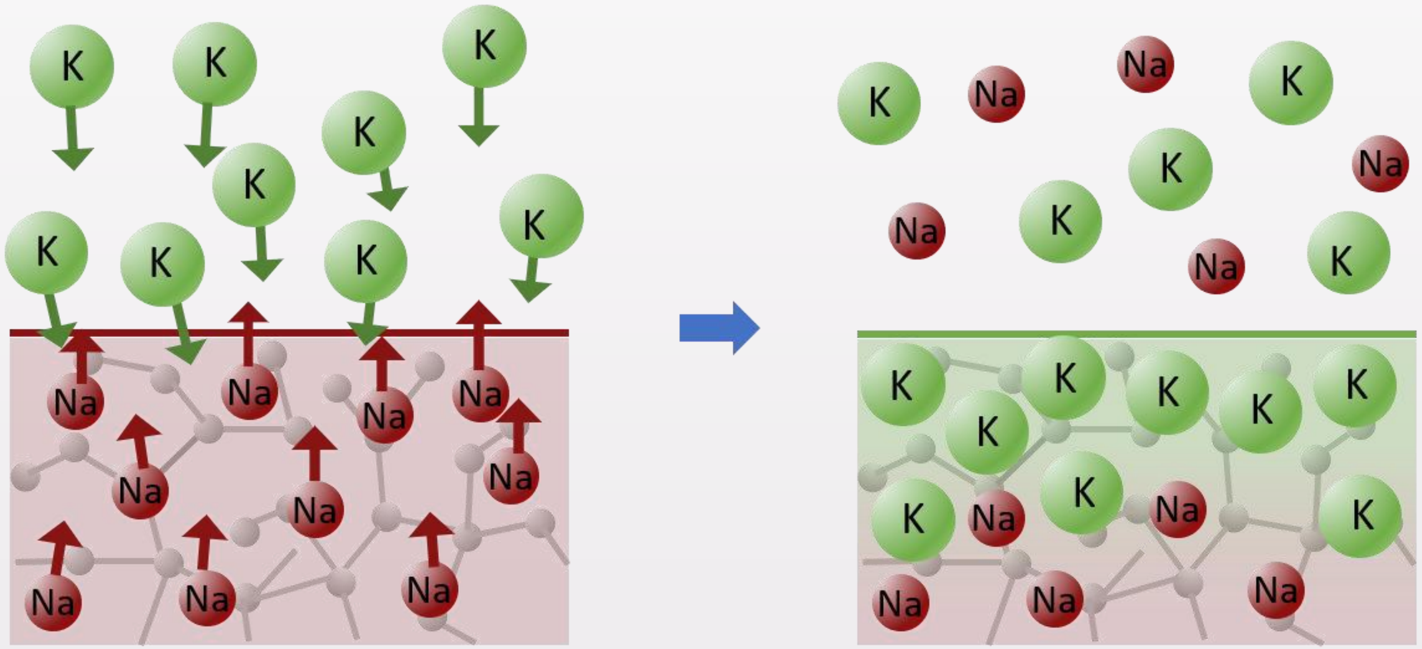


Merci !

PRINCIPLE OF IONIC EXCHANGE

During ionic exchange

After ionic exchange



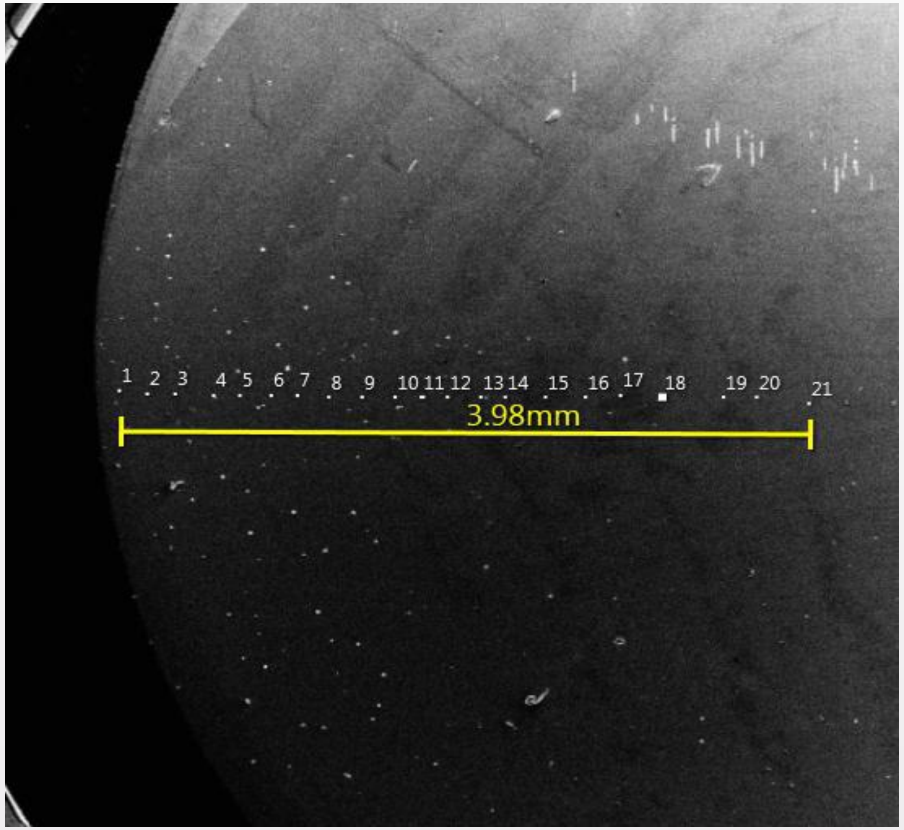
Double migration :

←Alkaline ions from the glass to the bath

→Alkaline ions from the bath to the glass

Variation of the chemical composition → ***Variation of the refractive index***

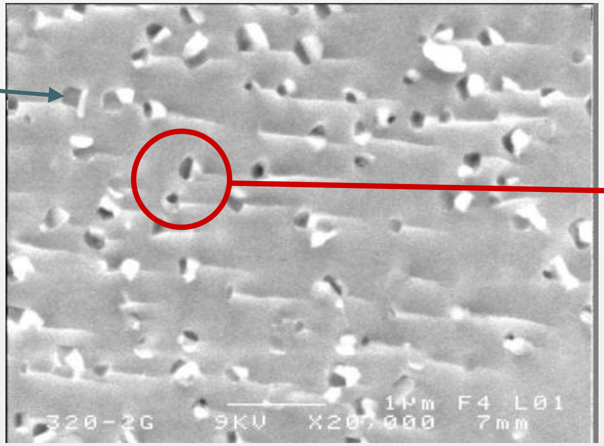
Chemical analysis by EDS measurements

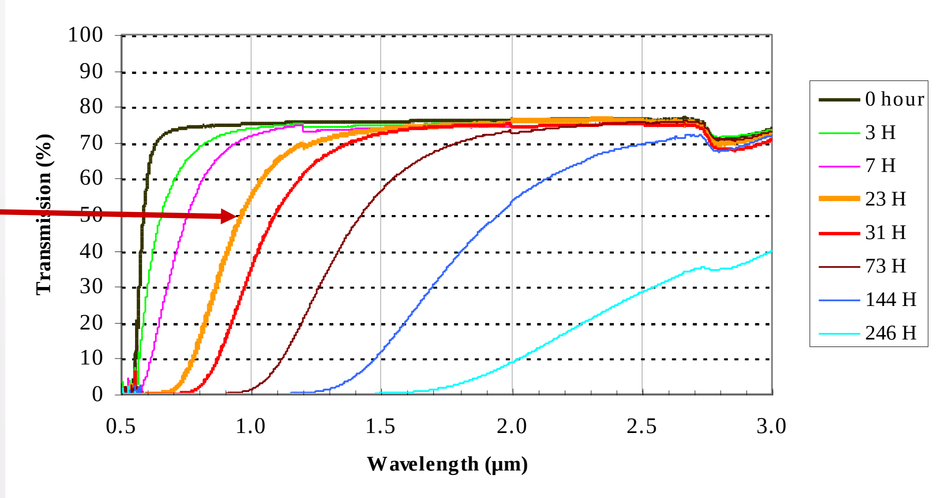


Gives us the atomical percent of each elements in the glass along a line of dots

Base glass (0h) *Heat treatment at 290°C* ***(Tg+30°C)****, growing time* → ***487h***

CsCl crystals (100nm)



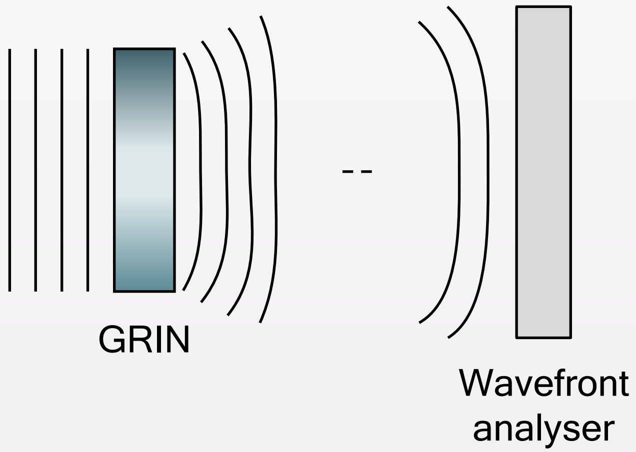


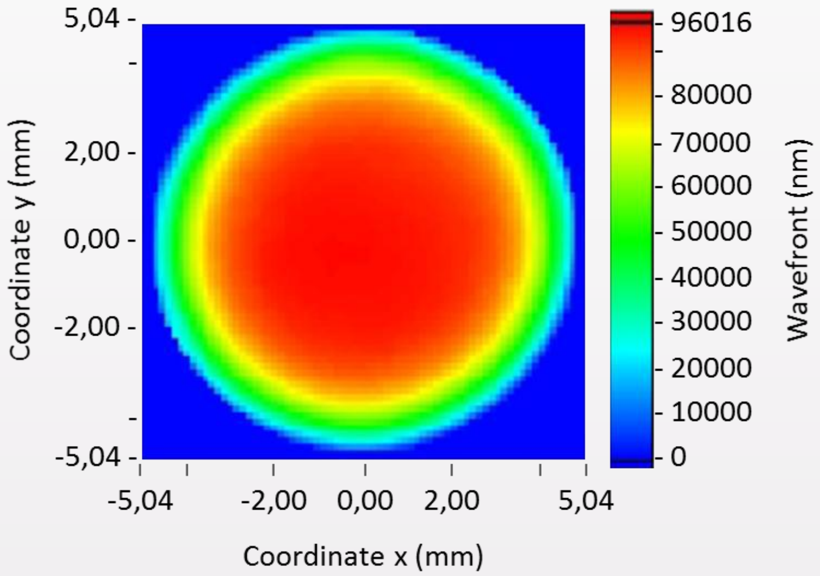
- Shift of the beginning of transmission by **scatterings**
- Excellent transmission in the infrared up to 11,5 µm

➡ **No changes of refractive index after crystallization**

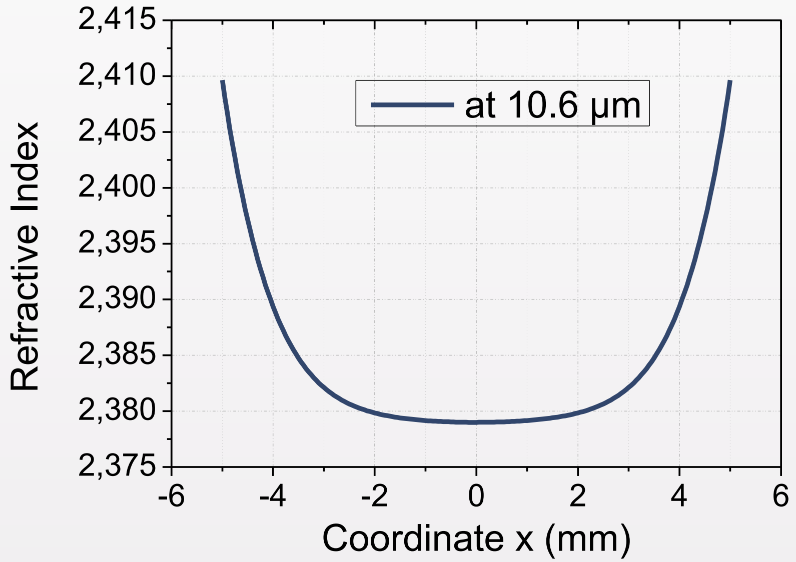
Applied the process on 80 $GeSe_2$ – 20 Ga_2Se_3 to obtain radial crystallization

Measure Δn of the glass-ceramic through Wavefront analyzer at 10.6 µm





Wavefront delay

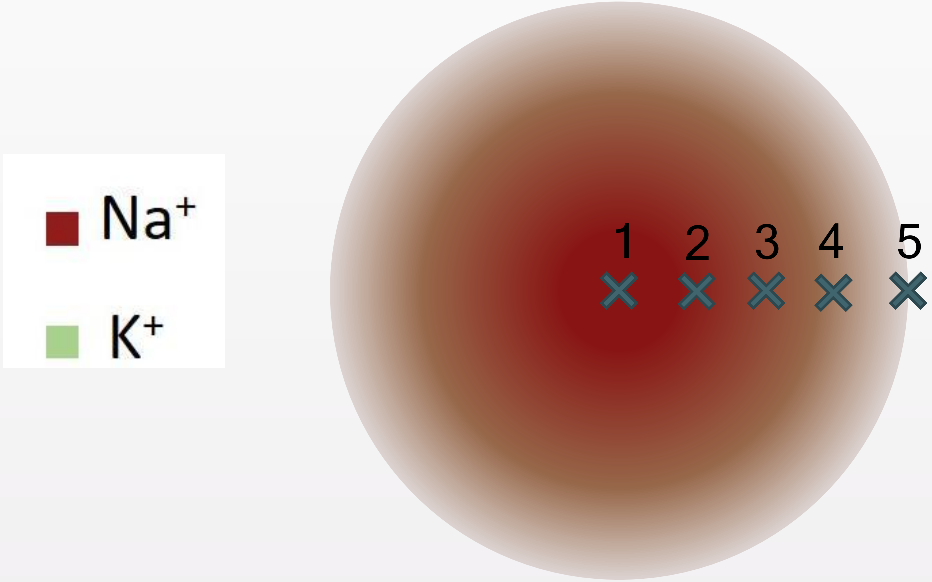


Profil Index calculated

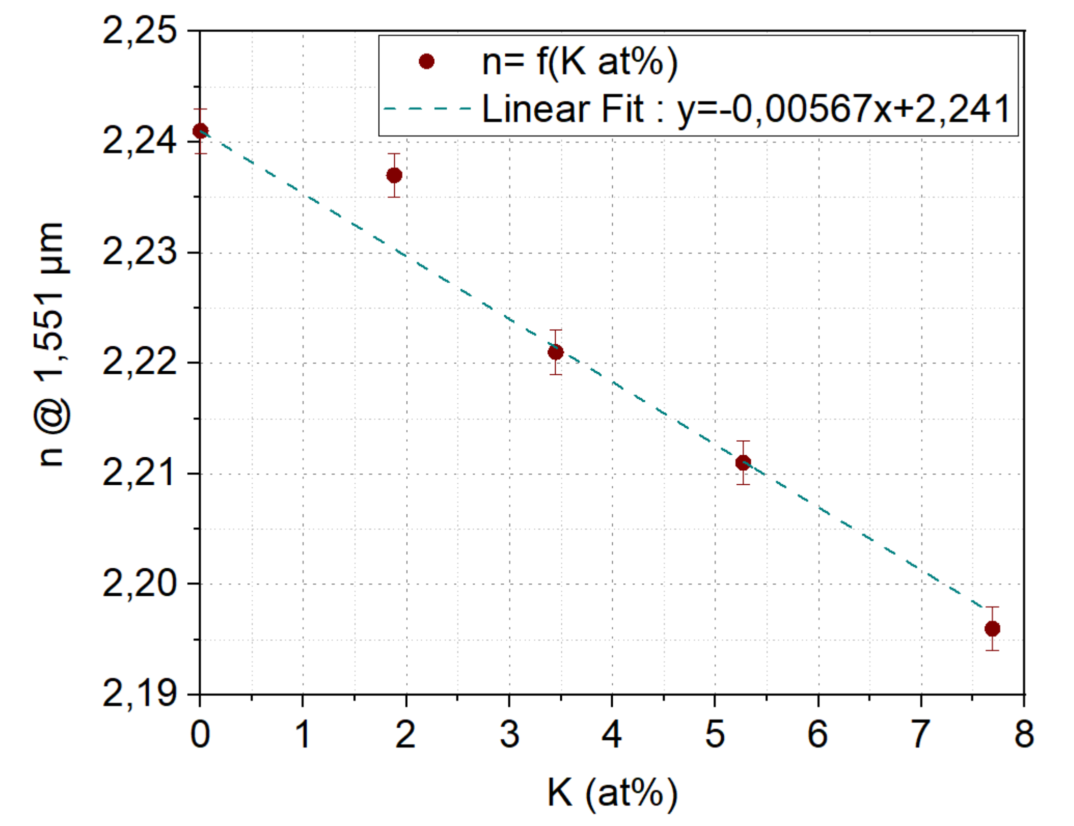
$$\Delta n_{measure} = 0.03 \pm 2.10^{-3}$$

Corresponding to homogeneous crystallization :
Δn = 0,032

Index profile estimation by synthesis of different compositions



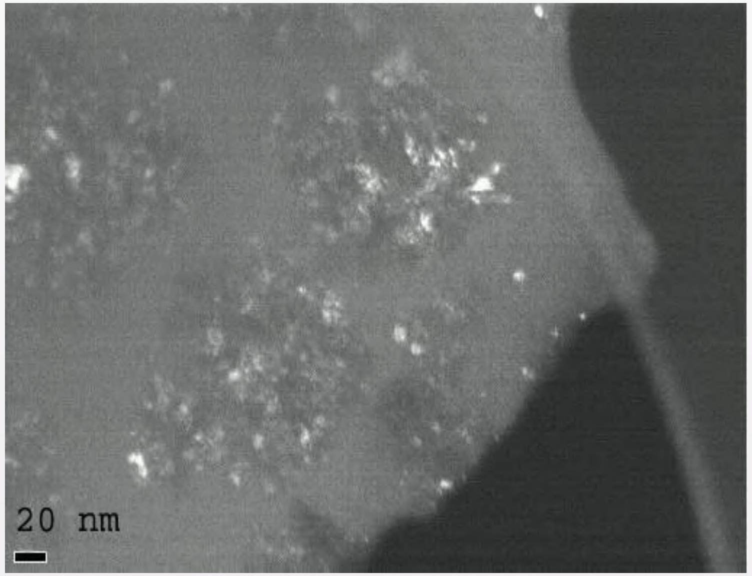
Index measurement @ 1,551µm

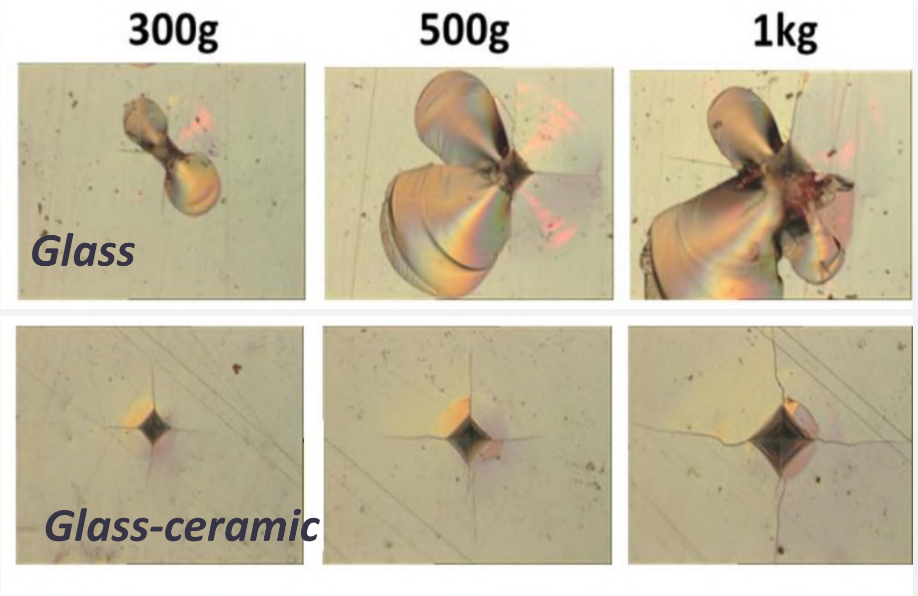


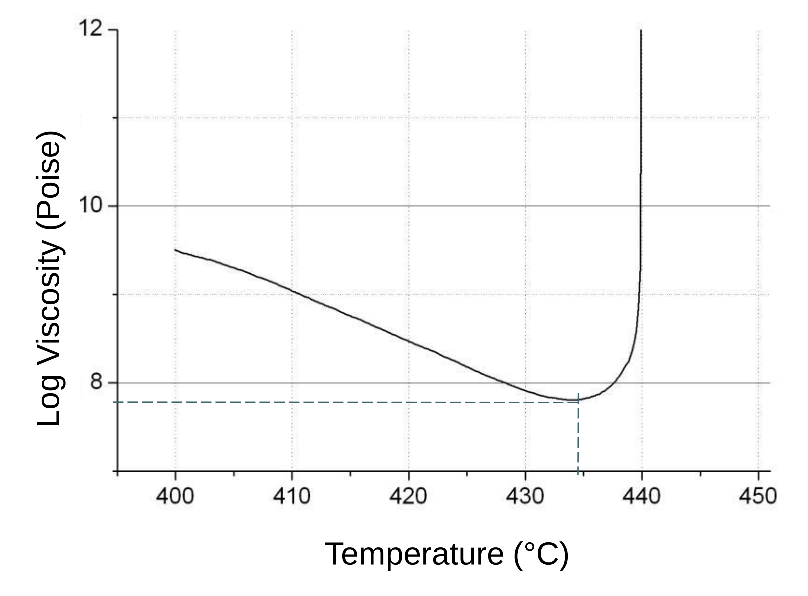
1. $(72\ GeSe_2 - 28\ Ga_2Se_3)_{75}\ (NaI)_{25}$
2. $(72\ GeSe_2 - 28\ Ga_2Se_3)_{75}\ (NaI_{0,75}\ KI_{0,25})_{25}$
3. $(72\ GeSe_2 - 28\ Ga_2Se_3)_{75}\ (NaI_{0,5}\ KI_{0,5})_{25}$
4. $(72\ GeSe_2 - 28\ Ga_2Se_3)_{75}\ (NaI_{0,25}\ KI_{0,75})_{25}$
5. $(72\ GeSe_2 - 28\ Ga_2Se_3)_{75}\ (KI)_{25}$

Δn max = $-4{,}5.10^{-2}$

➢ *Development of abrasion-resistant IR optics*







Nanoparticules of (5nm), aggregate (100nm)
Phase separation

Thermo-mechanical properties strongly enhanced

Combination between crystallization and shaping must be well controlled