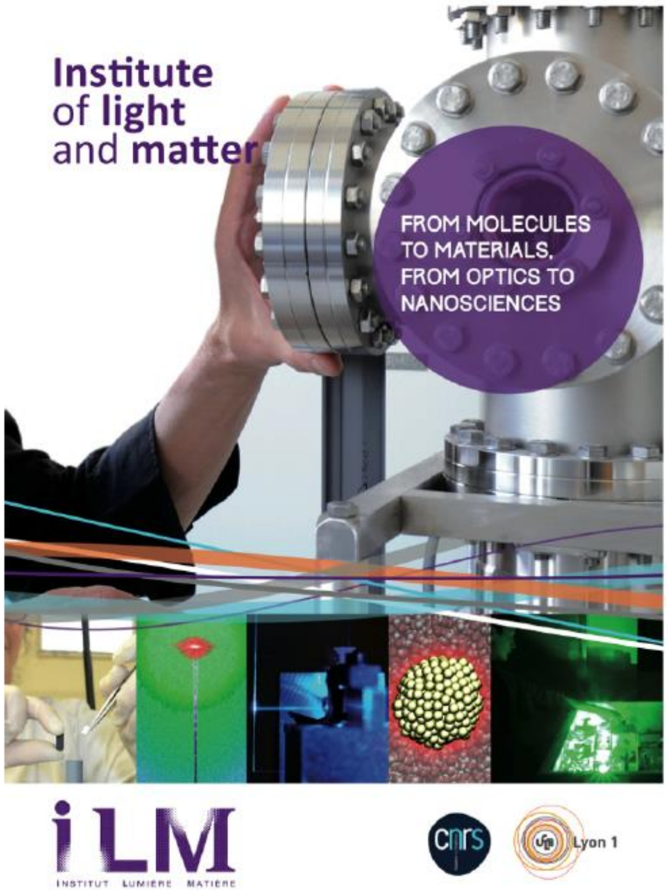
SINGLE CRYSTALS GROWTH AND CRYSTALS PERFORMANCE FOR OPTICAL AND LASER APPLICATION

Guillaume Alombert-Goget, Abdeldjelil Nehari, Omar Benamara, Valerii Kononets, Kherreddine Lebbou

Univ Lyon, Université Claude Bernard Lyon 1, CNRS, Institut Lumière Matière, F-69622, Villeurbanne, France



- Director: Dr. Philippe Dugourd
- An Interdisciplinary center of excellence based on synergy among Physics, Chemistry and their interfaces
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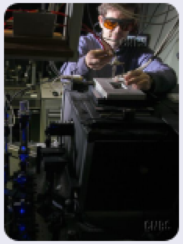
  - Soft matter & interfaces
  - Materials, Energy & Photonics
  - Nanosciences
  - Optics & Ultra-fast dynamics
  - Theory & Modeling

The Luminescence group, Prof. C.Dujardin

Nanoluminescence

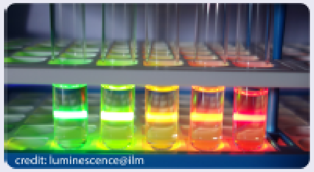
- F.Kulzer, A.Berthelot & J.Houel*
- Confocal, Q-dots, blinking, single-particle . . .

Sensor



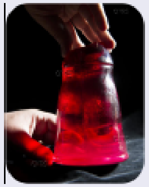
- G.Ledoux*, E.Homeyer & A.M.Jurdyc
- T & P contact-less probes, micro-fluidics . . .

Synthesis & processing



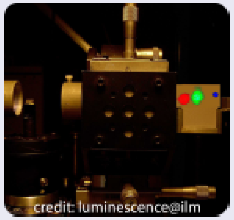
Colloïdal synthesis
B.Mahler*

Laser Ablation in Liquid
D.Amans



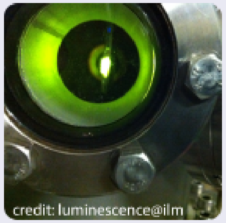
Crystal growth
K.Lebbou & G.Cagnoli

Lasers

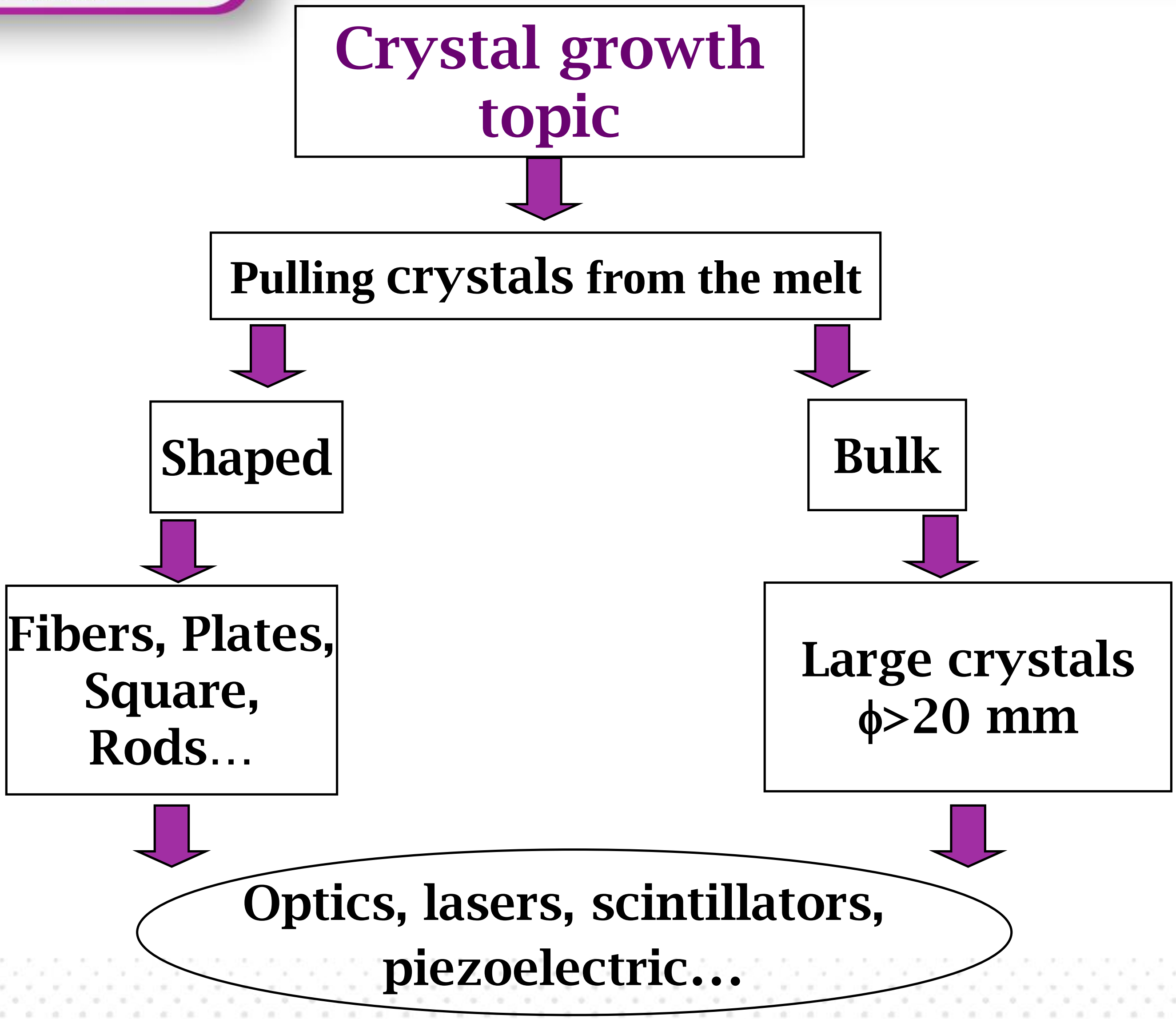


- A.Brenier, G.Boulon & Y.Guyot
- Bi-functional, non-linear, Yb^{3+} . . .

Scintillators



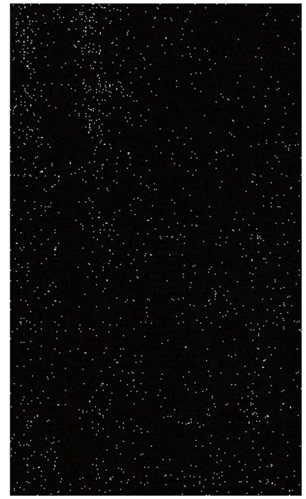
- A.Belsky
- theory, applications, crystals, fibers, films, nano . . .


Crystal growth topic
Pulling crystals from the melt
Shaped
Bulk
Fibers, Plates, Square, Rods…
Large crystals ϕ>20 mm
Optics, lasers, scintillators, piezoelectric…

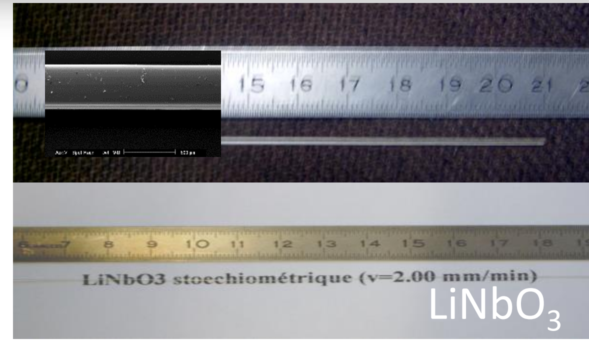
Crystal fibers

$KNbO_3$

KLN

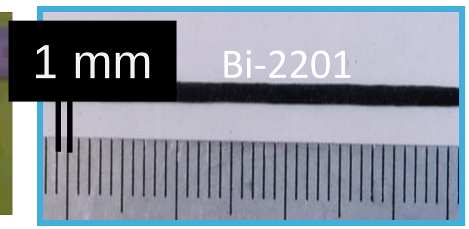


SBN



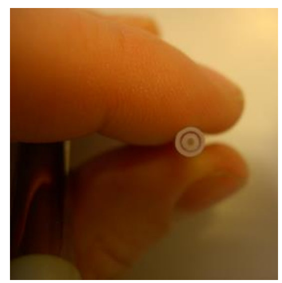
$LiNbO_3$

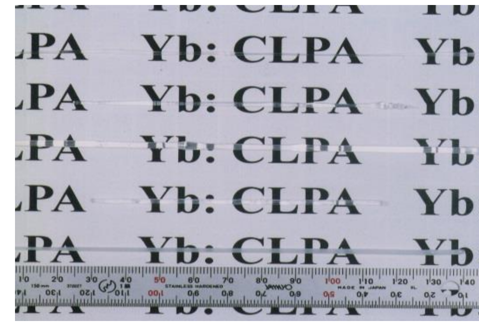
Bi-2212



1 mm

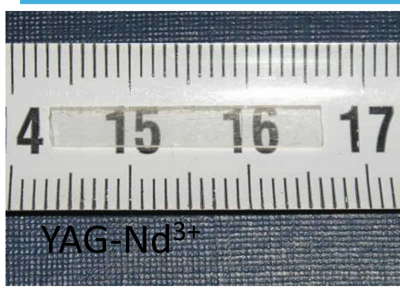
Bi-2201



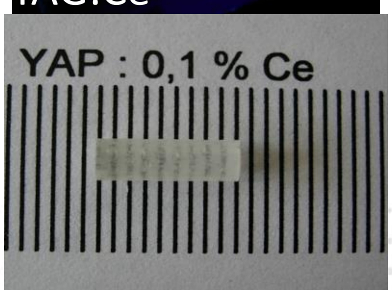


$Ca_8(La_{2-x}Yb_x)(PO_4)_6)_2$

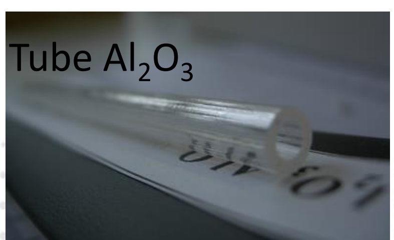
YAG:Ce



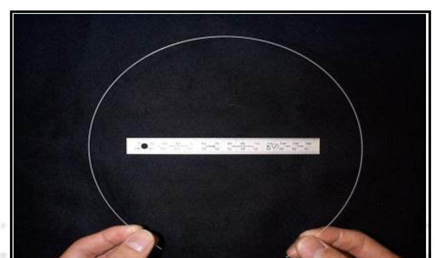
YAG-Nd^{3+}



YAP : 0,1 % Ce



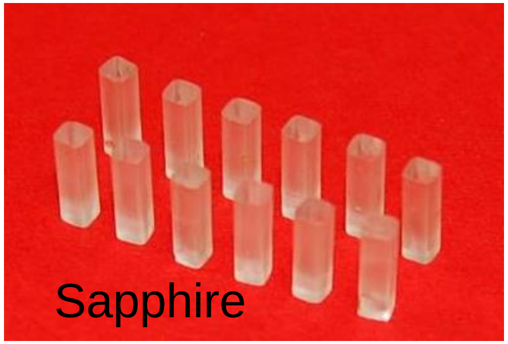
Tube Al_2O_3

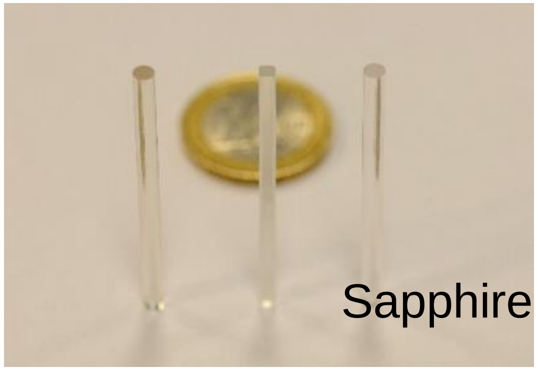


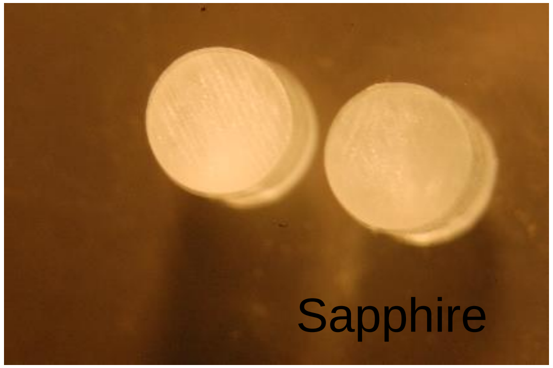
Y_2O_3- Al_2O_3 (eutectique)

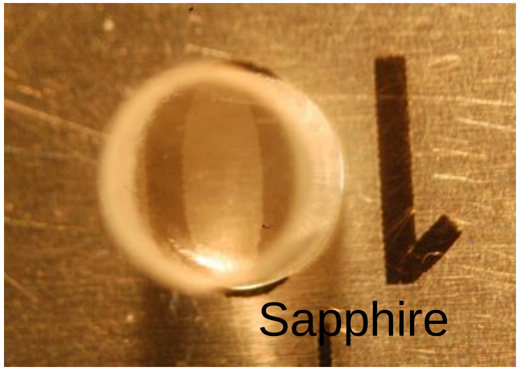
K.Lebbou et al

Cristaux saphir tirés par µ-PD

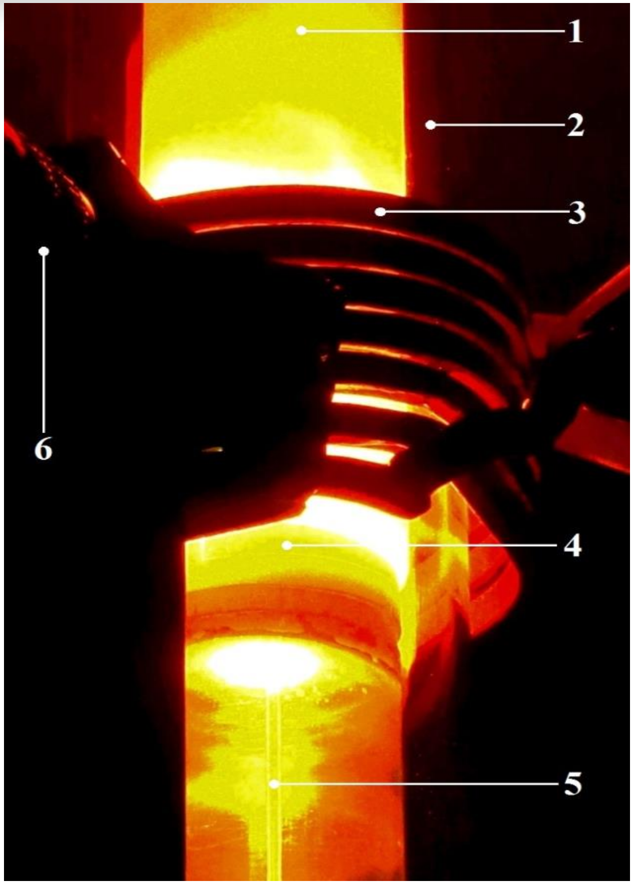








A

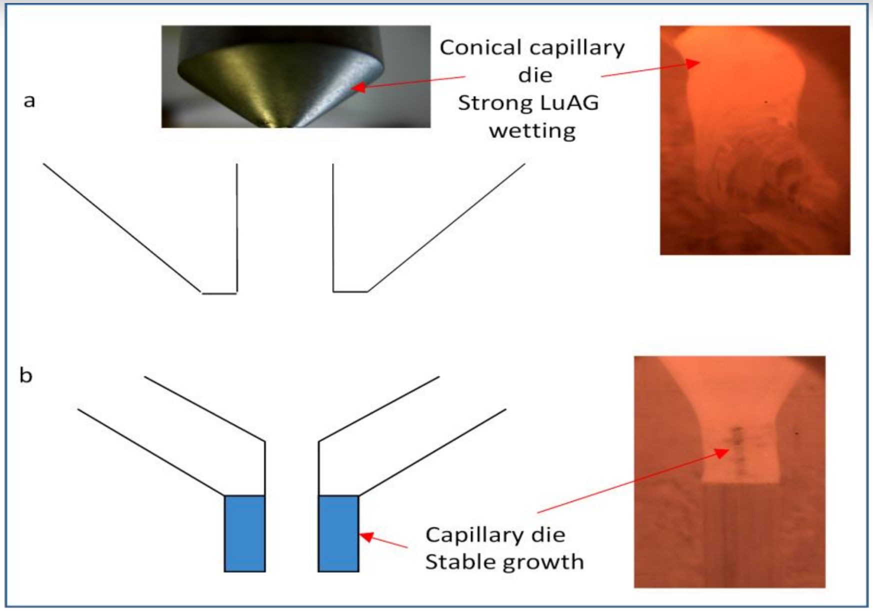


B

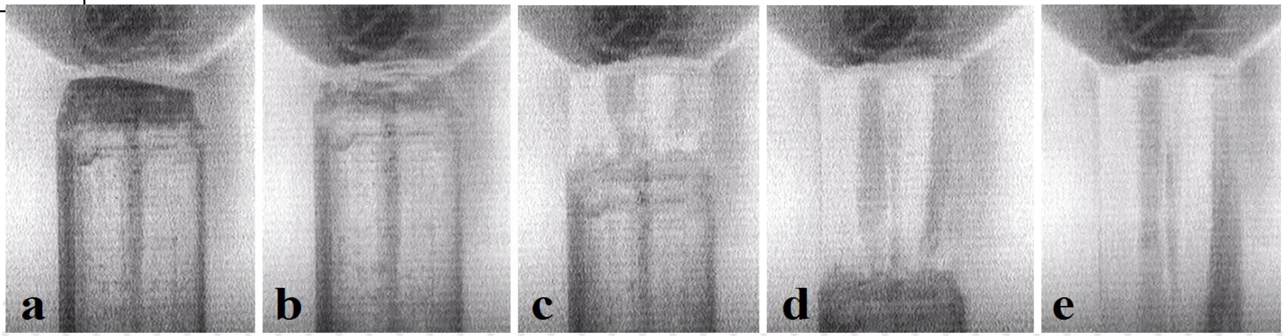
(a) (1 – thermal insulating ceramics, 2 – quartz tube, 3 – RF heating coils, 4 – hot zone, 5 – seed mounted on the motorized shaft, 6 – CCD camera)

(b) Machine for the fiber growth by µ-PD method

Crucible design for LuAG fiber growth

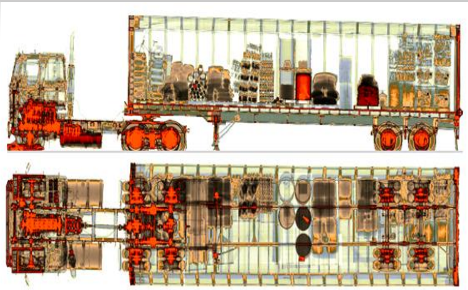


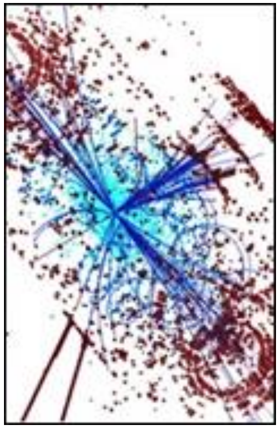
A) Instable growth (wetting)
B) stable growth (wetting controlling).

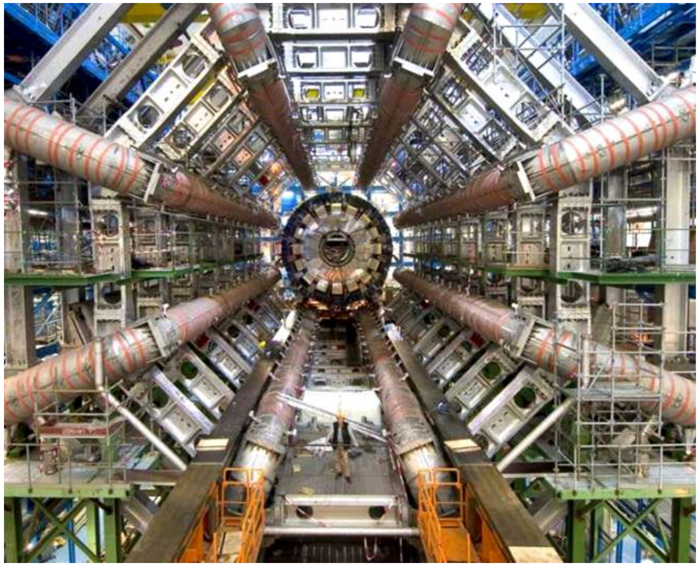


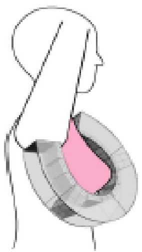
Seeding stages at YAG:Ce growth : seed moving towards the capillary (a), connection of the seed to the capillary L = 0 cm (b); L = 0.5 mm (c), L = 1.5 mm (d), L = 2 mm (e).

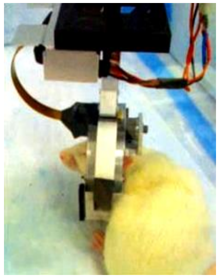
cintillation crystals applications







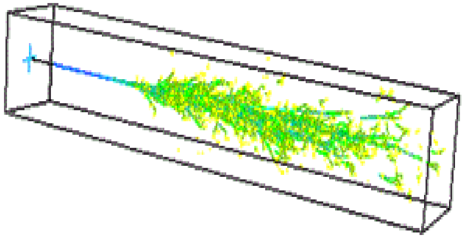




Medical diagnostics devices

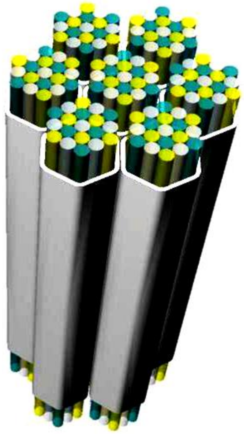
Border control and security systems

High energy physics

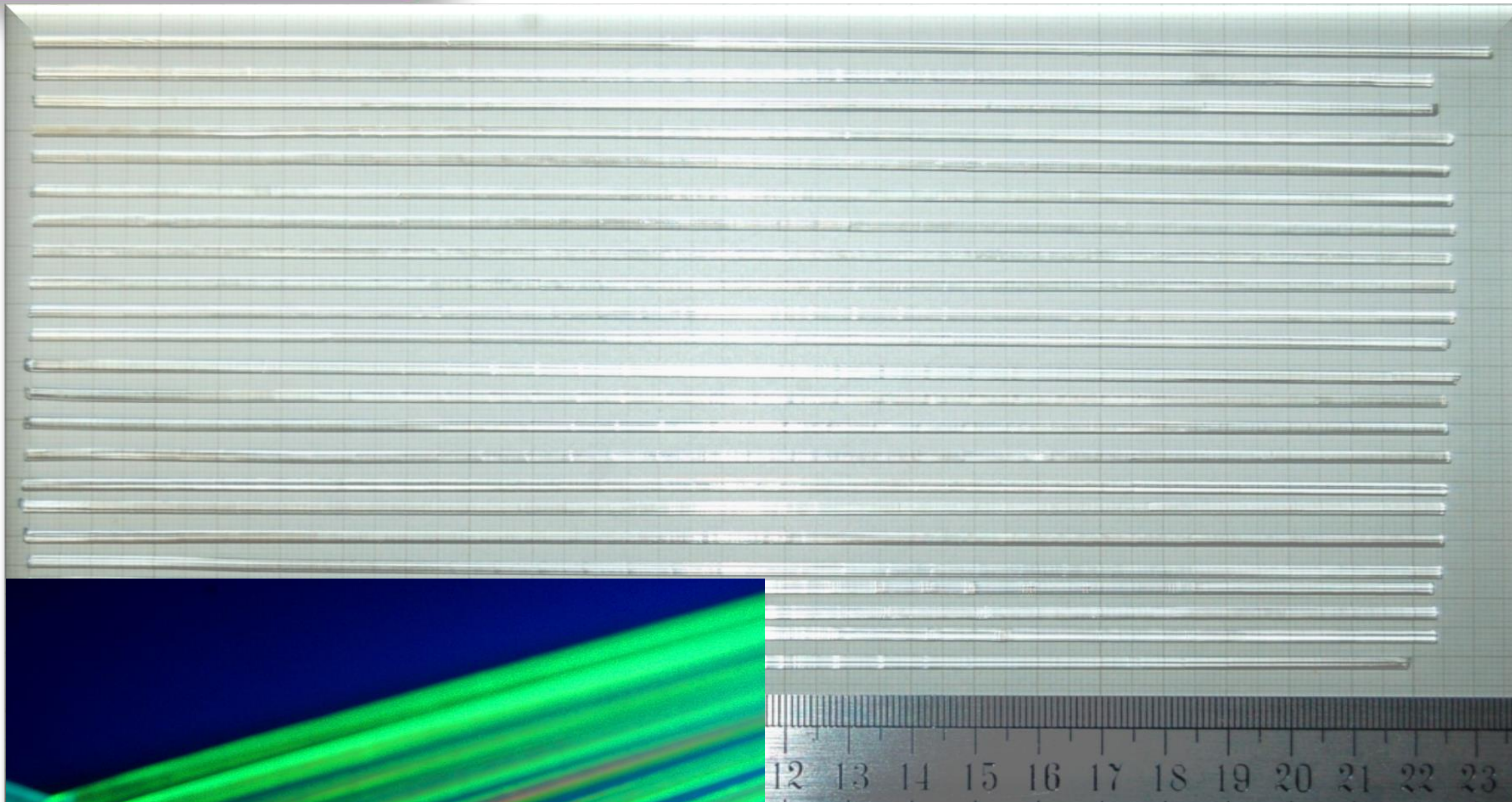


LHC → **HL-LHC**

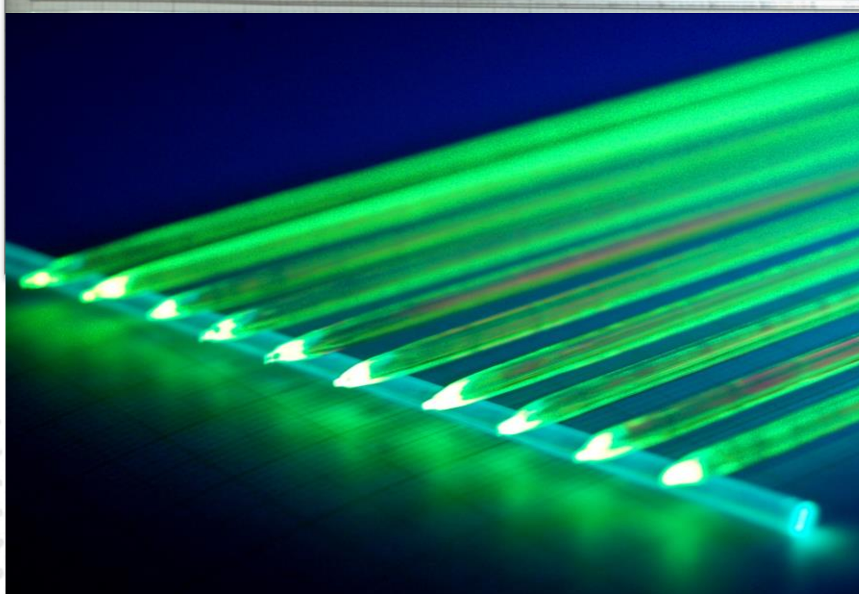
Bulk crystals | **Fibers**



LuAG FIBERS GROWTH



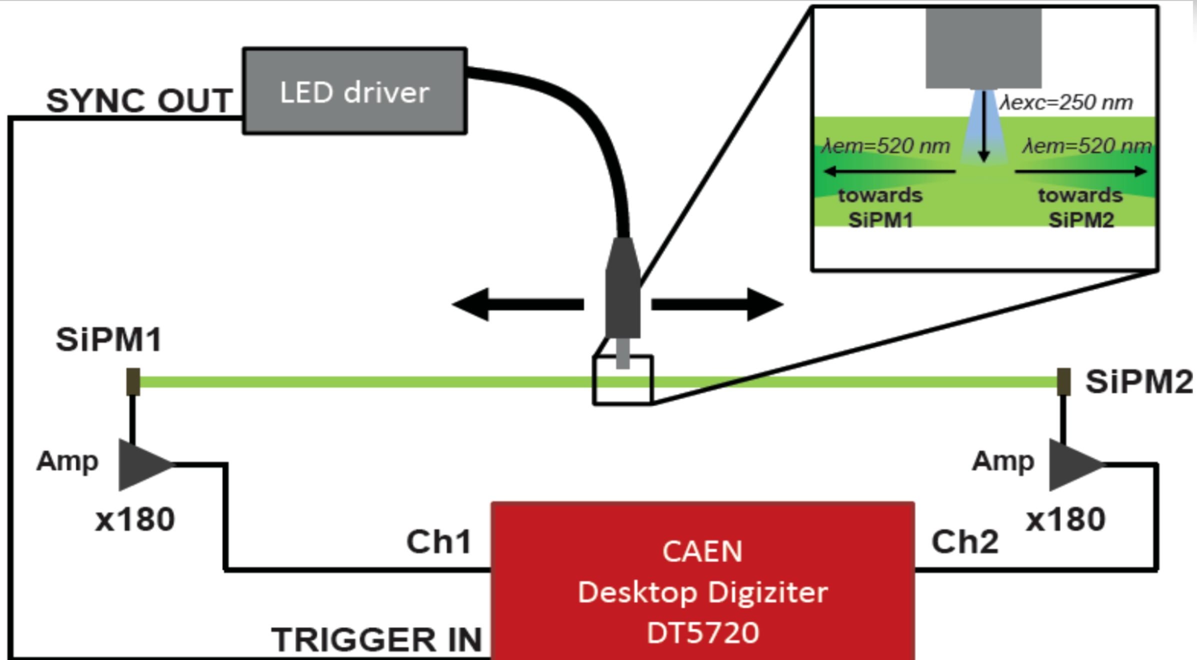
Undoped LuAG fibers (over 22 cm)

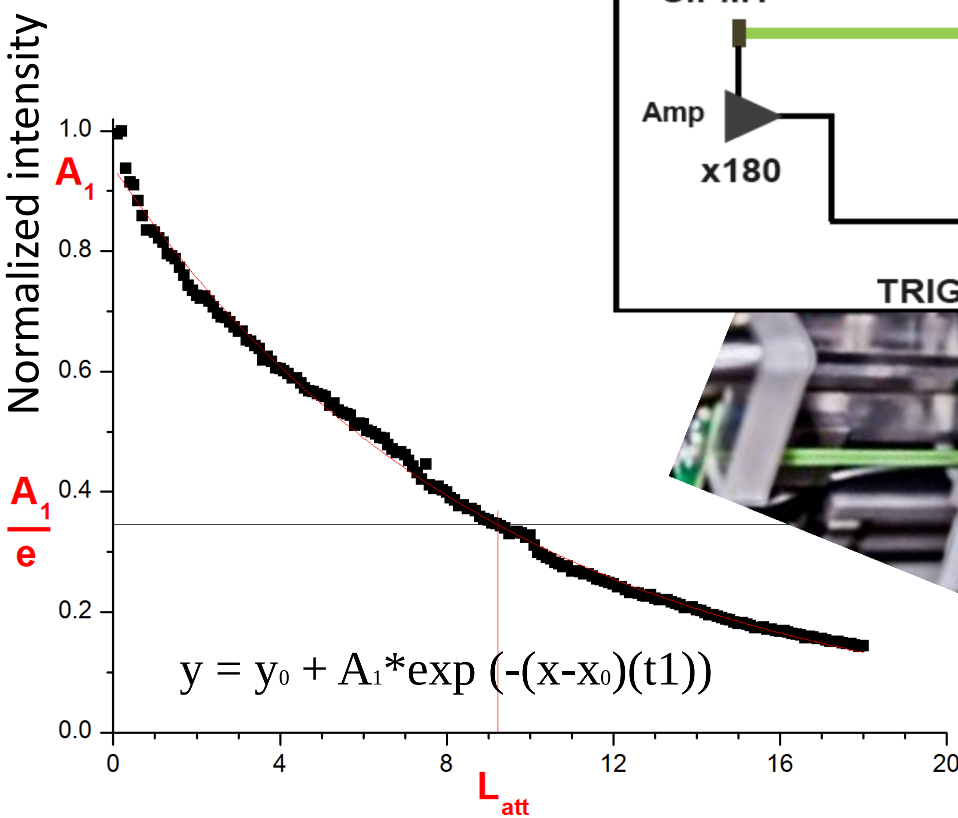


Ce-doped LuAG fibers (over 22 cm)

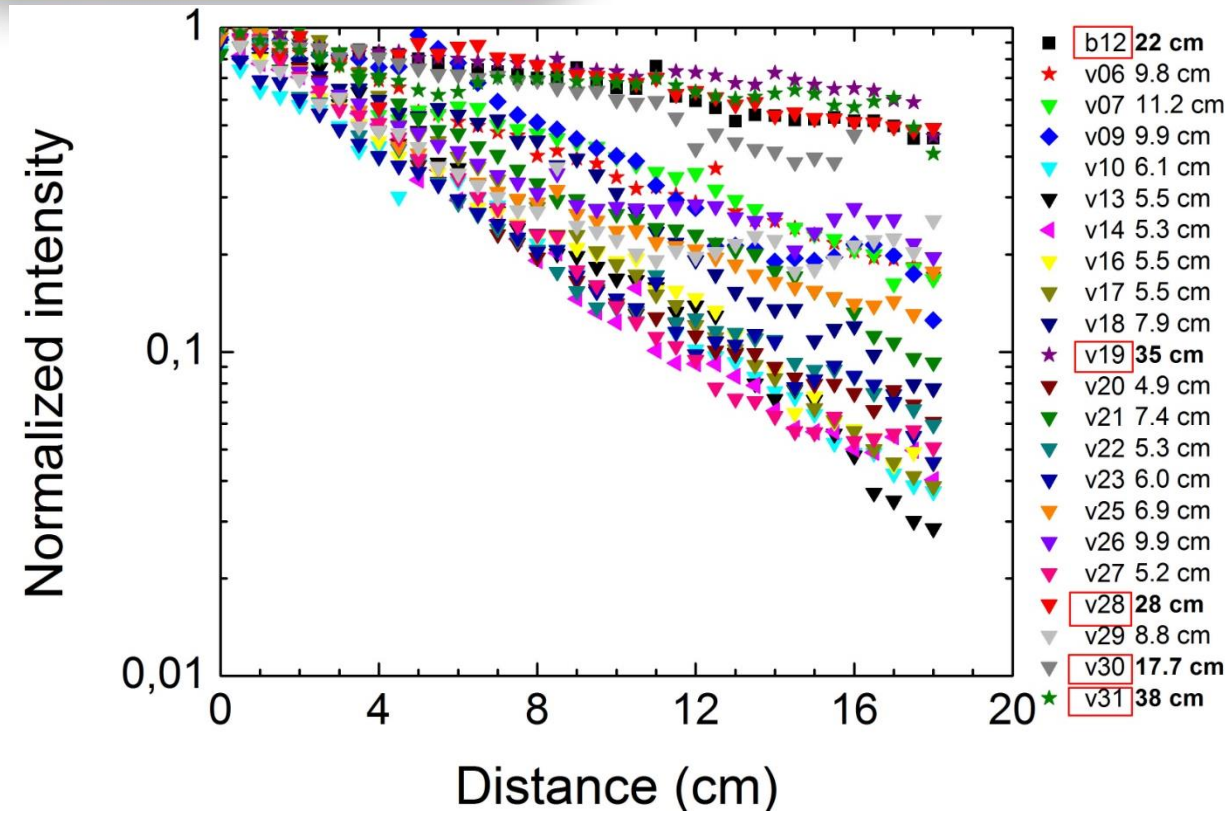
ATTENUATION LENGTH MEASUREMENTS IN GARNET FIBERS

Setup for the measurement of light attenuation of the fibers (LED bench) in CERN

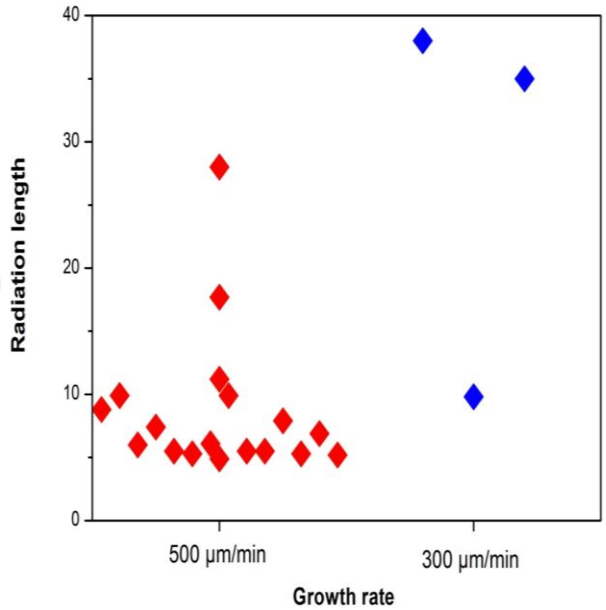




Calculation of attenuation length in fibers

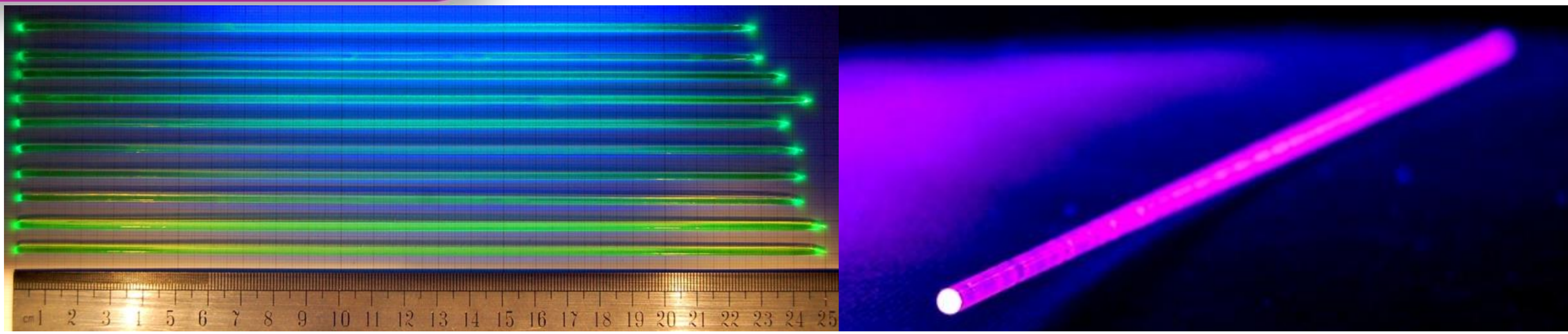


The averaged results give 8.7 cm attenuation length for fibers grown at 500 µm/min
and 27.6 cm at 300 µm/min

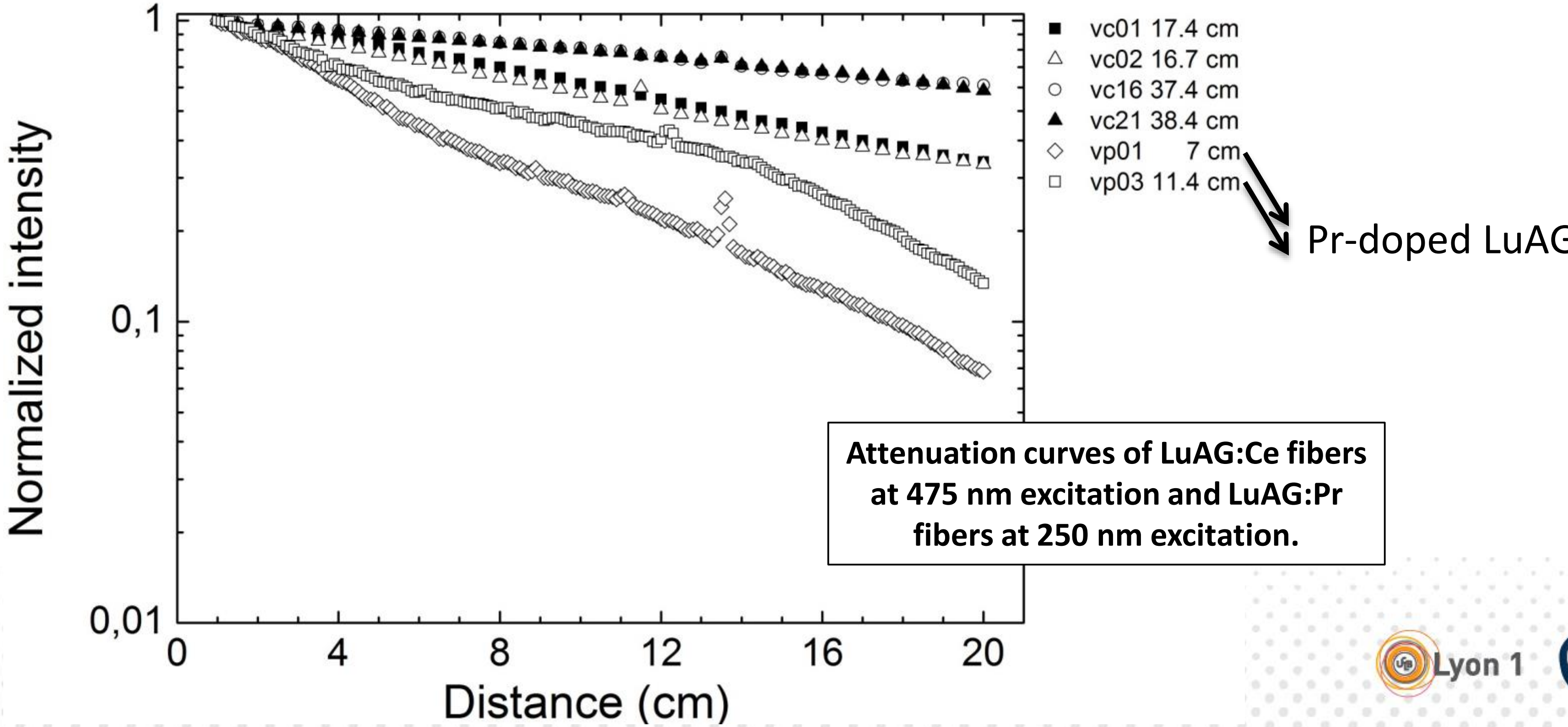


LuAG attenuation curves 475 nm excitation normalized by their maxima. The attenuation lengths are quoted in the legend.
Fibers grown with at 350 µm/min – "quadrates",
300 µm/min – "stars",
500 µm/min – "triangles",
500 µm/min grown with [100] seed – "rhombs"

LuAG:Ce and LUAG:Pr FIBERS



LuAG:Ce (left)and LuAG:Pr (right) fibers with lengths over 22 cm under UV light (V = 300 µm/min)



Attenuation curves of LuAG:Ce fibers at 475 nm excitation and LuAG:Pr fibers at 250 nm excitation.

EFFECT OF THERMAL ANNEALING OF LuAG AND LuAG:Ce FIBERS

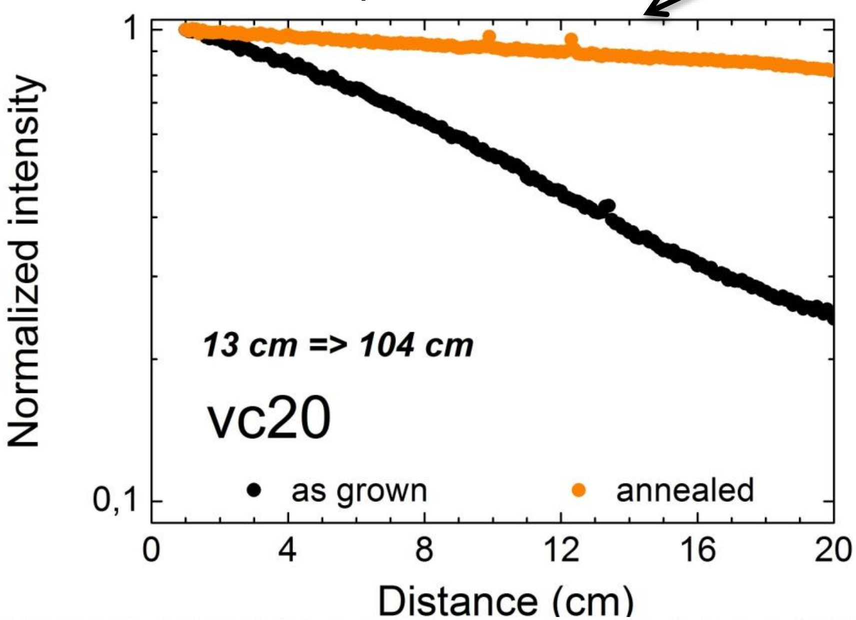
Crystal		LuAG				LuAG:Ce			
Growth rate, µm/min		300		500		300		500	
Growth orientation		[100]	[111]	[100]	[111]	[100]	[111]	[100]	[111]
Radiation length, cm	Before	15	21	9,5	29	13	17	13	18
	After	14	11	7	24	**104**	**50**	**14**	**23**

nnealing regime:

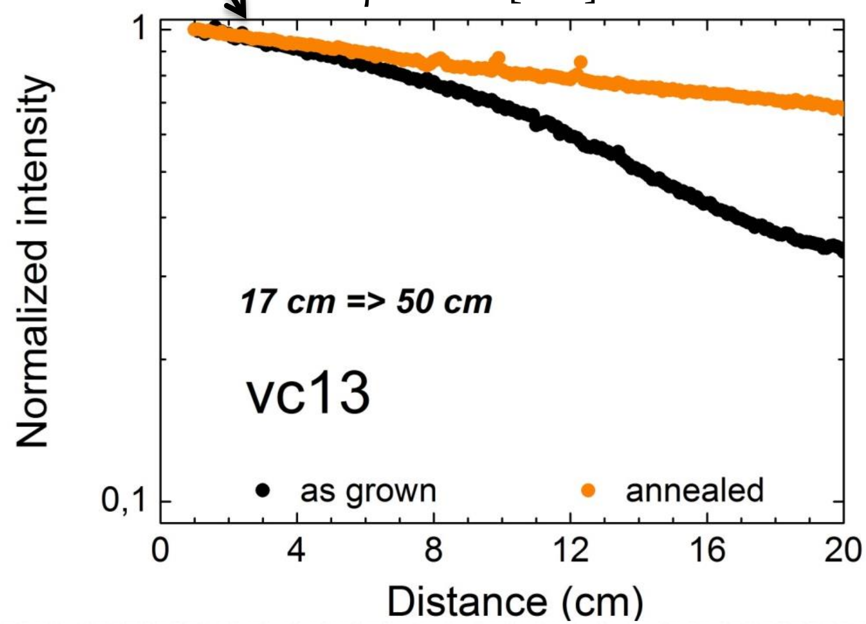
for . hours

The request is:
minimum 40 cm
attenuation length

300µm/min [100]

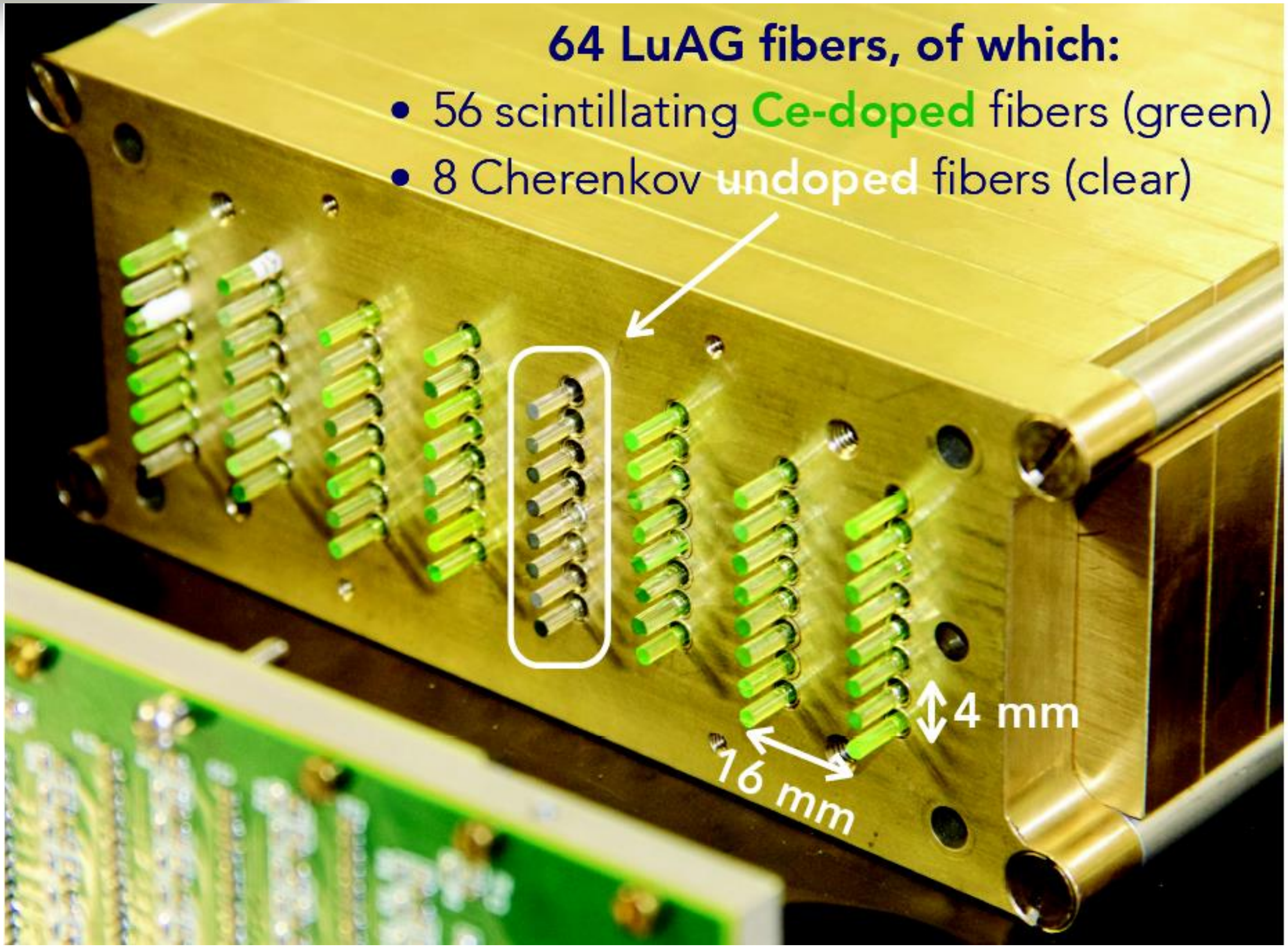


300µm/min [111]



Effect of annealing on attenuation of the LuAG:Ce fibers at 475 nm excitation.
The attenuation lengths are indicated.

LuAG and LuAG:Ce FIBERS TESTING



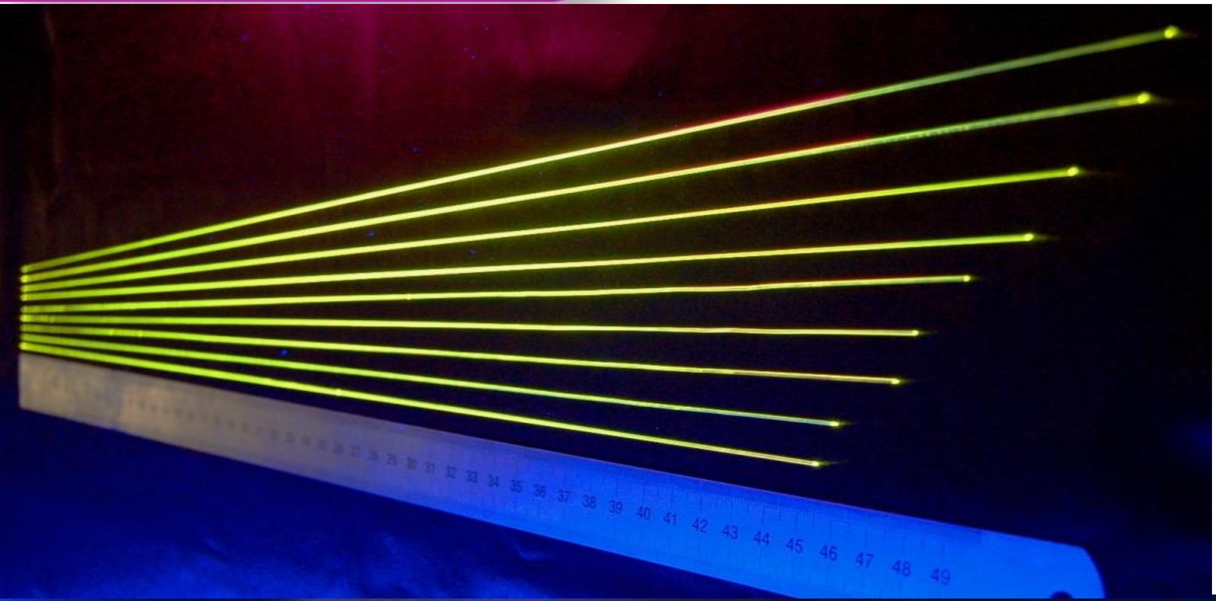
Photos of the calorimetric module.

[7] M. Lucchini,….V. Kononets... et al// Proceedings of the IEEE NSS/MIC, Seattle, WA USA 8-15 November 2014, Report N47-1. http://www.npss-confs.org/nss/program/ListProgramDB.asp?session=N47

Now we are working on

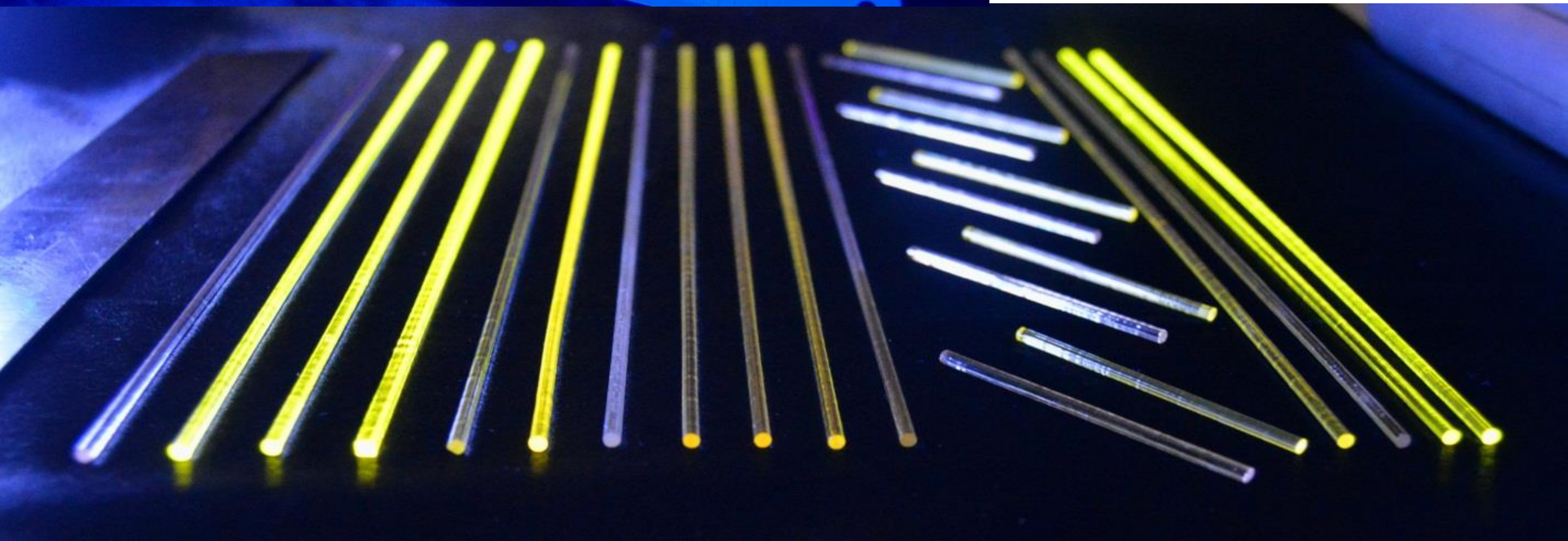
- Growth of YAG-based fibers
- Selection of the optimal growth conditions, concentration of activator, post growth treatment
- Attenuation length, decay time, light yield measurements and microscopy

The aim is to reduce the decay time and to improve the attenuation length of YAG:Ce fibers as a cheaper concurent to LuAG



YAG:Ce fibers (1 mm dia, 45-60 cm length).

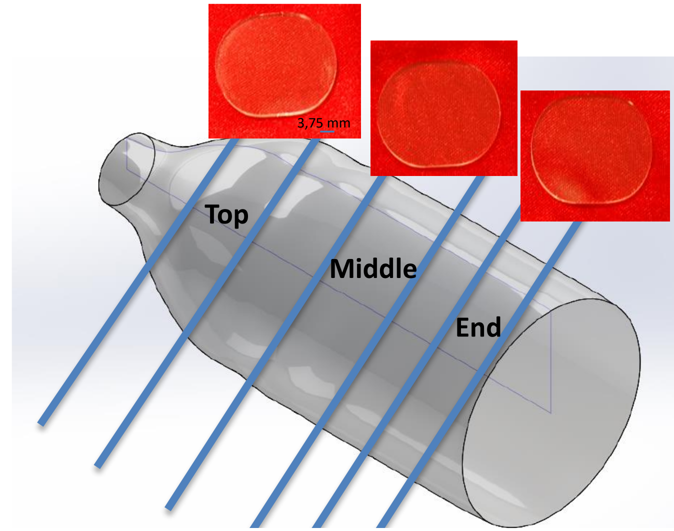
YAG:Ce, YAG,Mg fibers (2 mm dia, 2X2 square-shaped, 22 cm length).

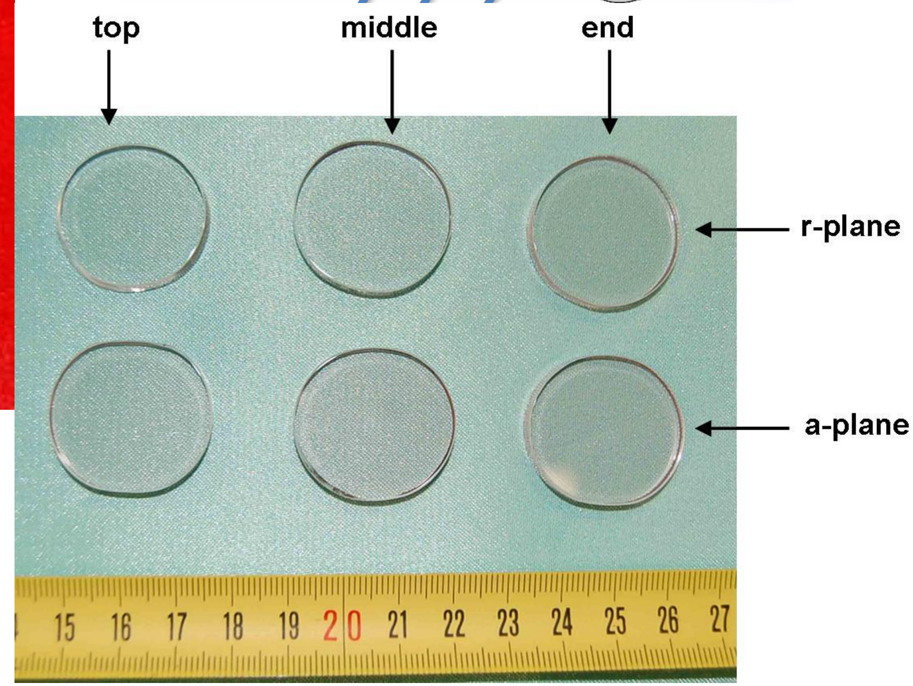


Bulk crystal

The grown crystals and samples

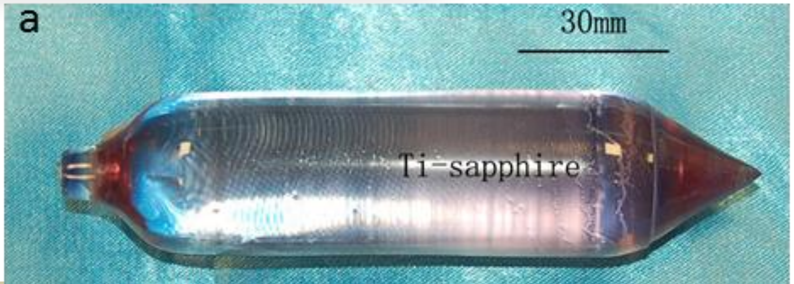
Cutting area for polishing and defects analysis



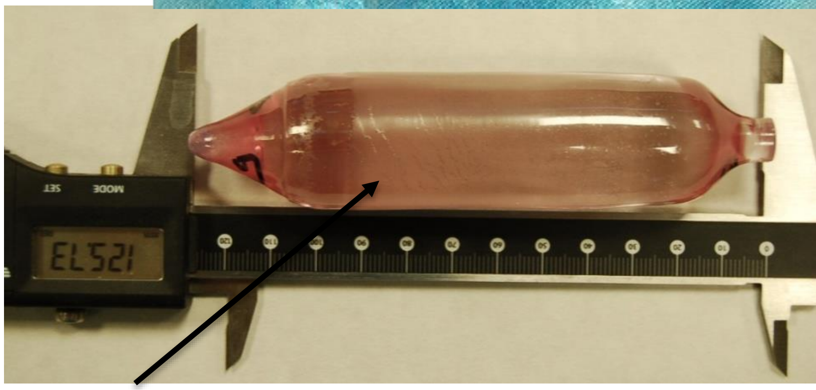


Some undoped sapphire crystals grown by Cz method

The grown Ti-sapphire crystals and samples

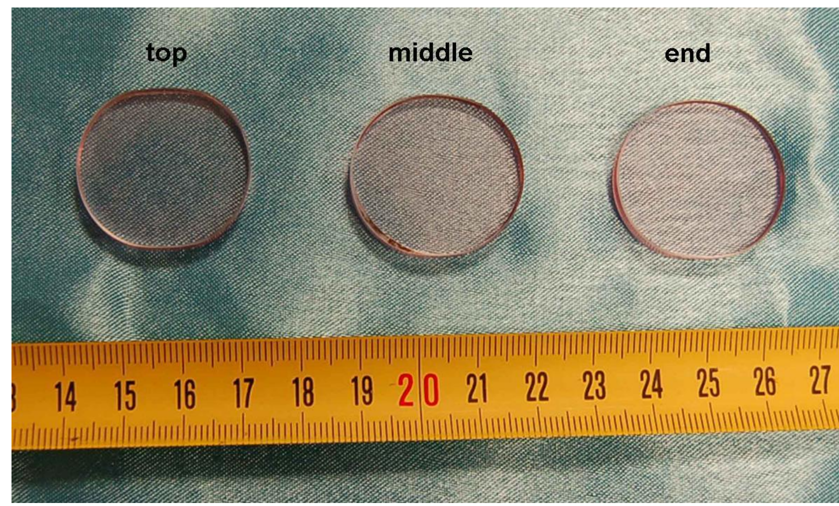


(a) CrysT1,r-axis, (b) CrysT3, a-axis.



CrysT5, r-axis (diameter 30 mm), titanium concentration 0.28 atom%

Optically polished Ti-sapphire wafers



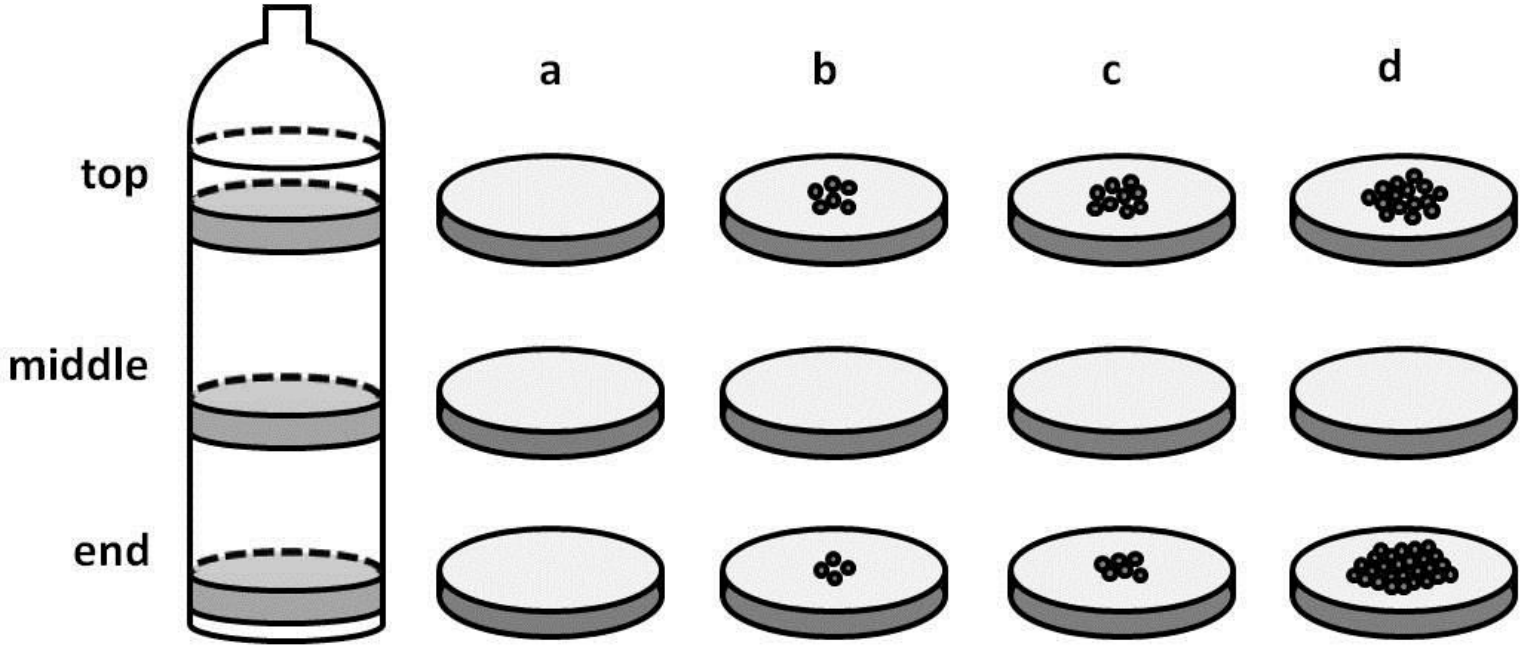
Bubbles and titanium segregation

CrysT7, a-axis, 4 mm/h, 8 rpm, Ti-concentration 0.5 atom%

The distribution of bubbles

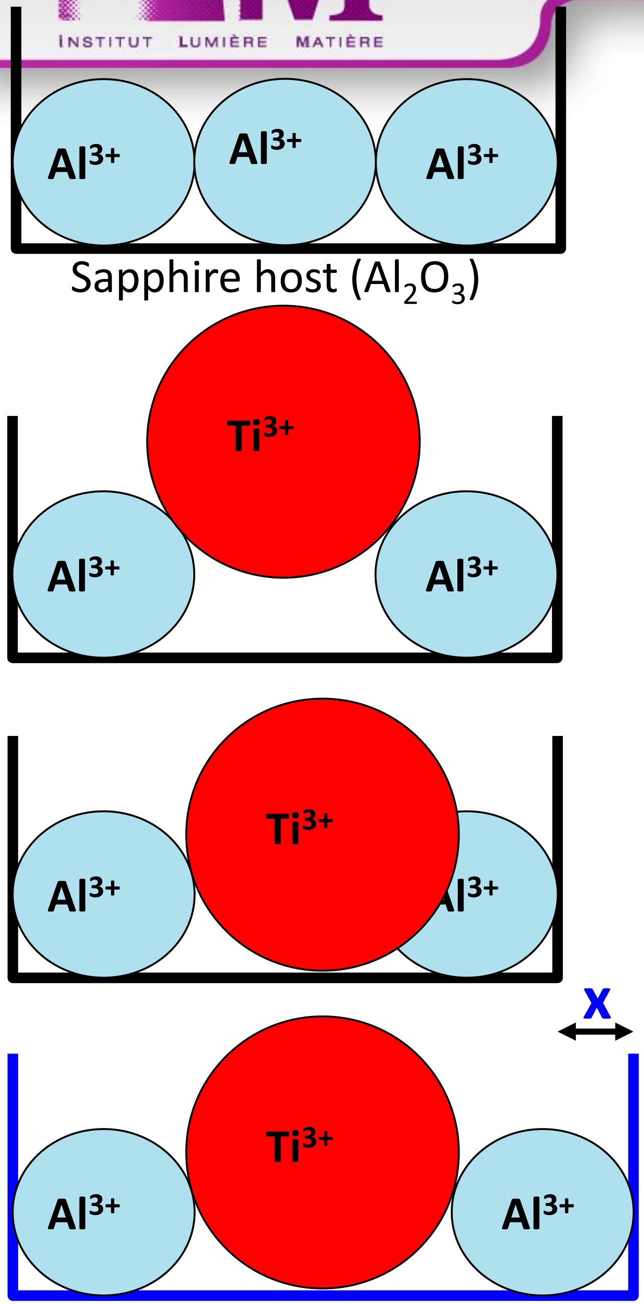
Schematic illustration of bubbles distribution

(a) T1, 1.5 mm/h, 8 rpm, 0.10 atom%; (c) T5, 4mm/h, 8 rpm, 0.28 atom%;
(b) T2, 2.5 mm/h, 8 rpm, 0.10 atom%; (d) T7, 4 mm/h, 8 rpm, 0.5 atom%.



The Ti-doped crystal grown at low pulling rate is bubbles free.
In the case of the crystals grown with high pulling rate, the bubbles are located in the core of top and end part.

Ti-dopant segregation



Ti incorporation in sapphire host

Substitution of Al^{3+} by Ti^{3+}

$Ti^{3+} > Al^{3+}$ ($\Delta r > 15\%$)

Segregation phenomena

Cell deformation

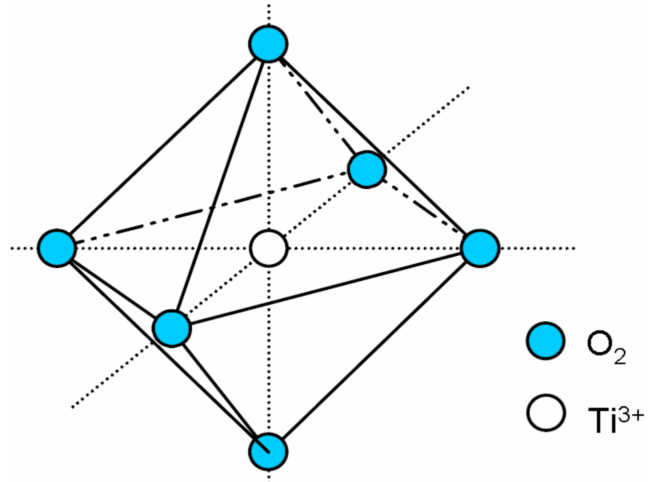
Hammer-hardening crystals

Crystal growth difficult

Lattice parameters variation

Deffects propagation

Optical quality degradation



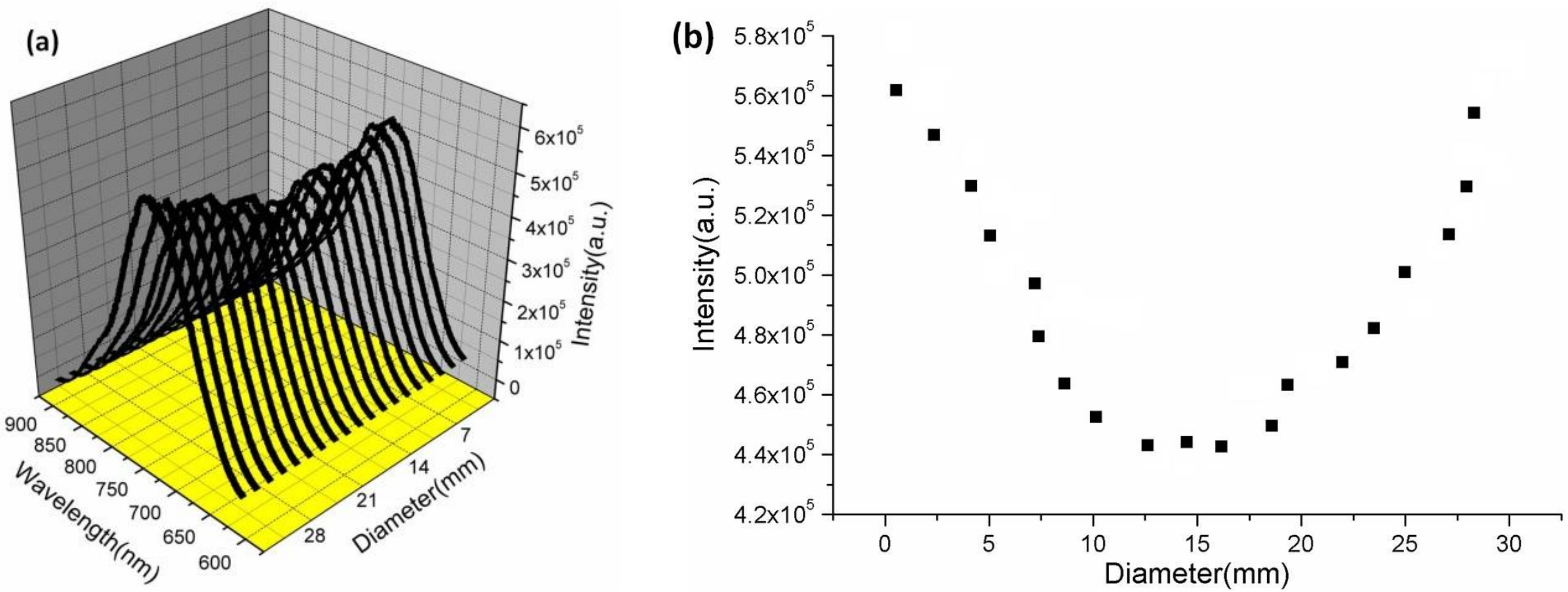
The solute concentration in the melt (C_l) increases

a solute concentration in the crystal increase along the pulling direction.

Ti-dopant concentration analysis by microlumienscense

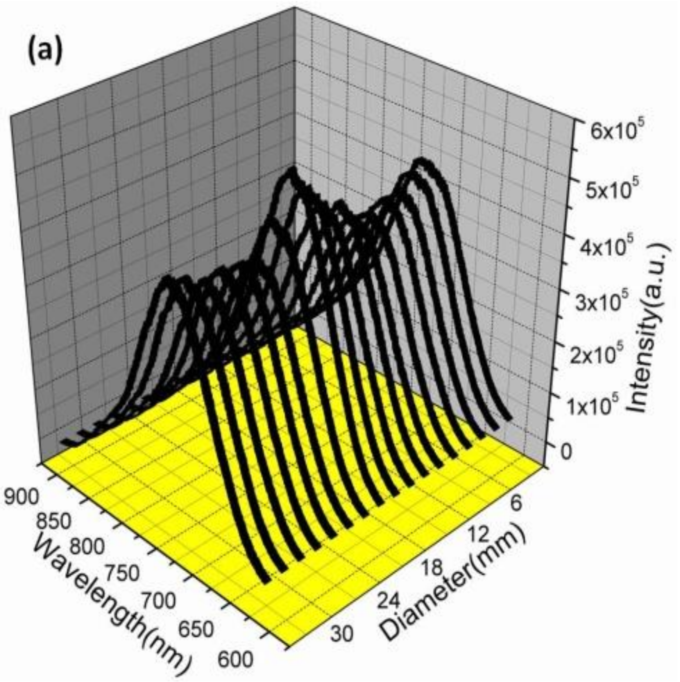
excitation of the Ti^{3+} luminescence at 532 nm

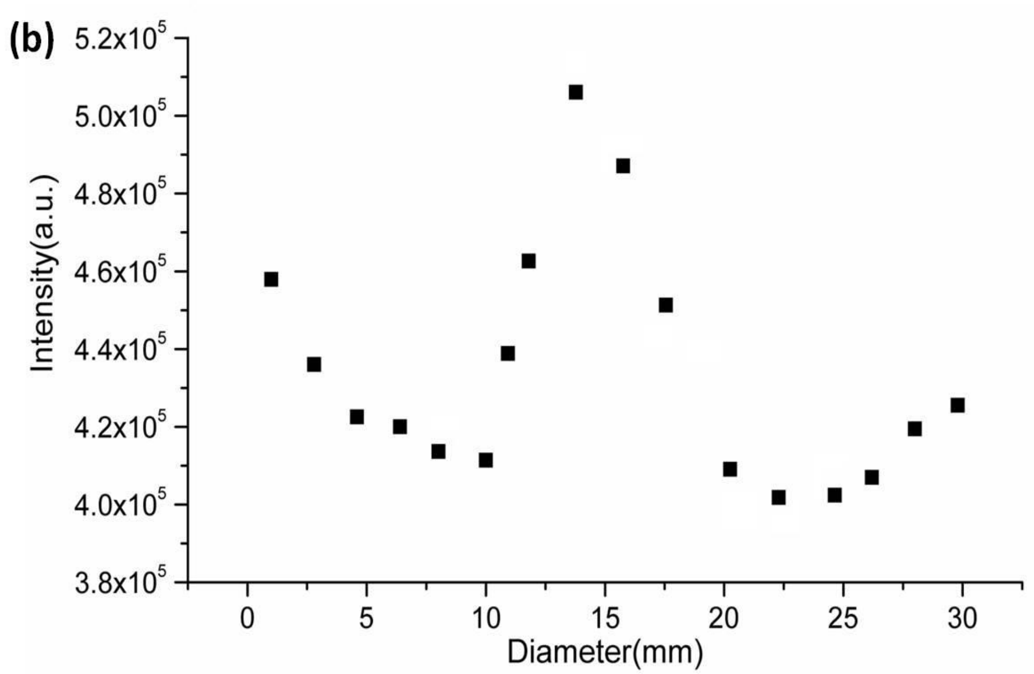
CrysT5, wafers without bubbles, titanium concentration 0.28 atom %.
(a) Microluminescence spectra recorded in different region of wafer
(b) Profile of the Ti^{3+} ion distribution in the as grown Ti-sapphire crystal



We assume that the variation of luminescence intensity is linear with the concentration of Ti^{3+} in the crystal.

CrysT5, wafers contain bubbles in the core, titanium concentration 0.28 atom%.





The destabilization of solid-liquid interface results from the titanium rejection, more titanium segregation result to more bubbles were captured in the core of crystals.

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Bubbles defects distribution in sapphire bulk crystals grown by Czochralski technique

H. Li, E.A. Ghezal, A. Nehari, G. Alombert-Goget, A. Brenier, K. Lebbou *

Institut Lumière Matière, UMR5306 Université Lyon 1-CNRS, Université de Lyon 69622 Villeurbanne cedex, France

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ABSTRACT

Sapphire crystals exhibit microscopic defects known as "micro-bubbles or micro-voids". We have studied micro-bubbles distribution, and their sizes in sapphire crystals grown by Czochralski technique. They are not uniform, depend on the pulling rate and their presence strongly affect the optical properties such as transmission and wavefront quality. The results provide important information about micro-bubbles distribution and the possibilities to minimize their propagation during the growth procedure of sapphire single crystal using Czochralski technique.

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Qualitative and quantitative bubbles defects analysis in undoped and Ti-doped sapphire crystals grown by Czochralski technique

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H. Li, E.A. Ghezal, G. Alombert-Goget, G. Breton, J.M. Ingargiola, A. Brenier, K. Lebbou *

Institut Lumière Matière, UMR5306 Université Lyon 1-CNRS, Villeurbanne Cedex, France

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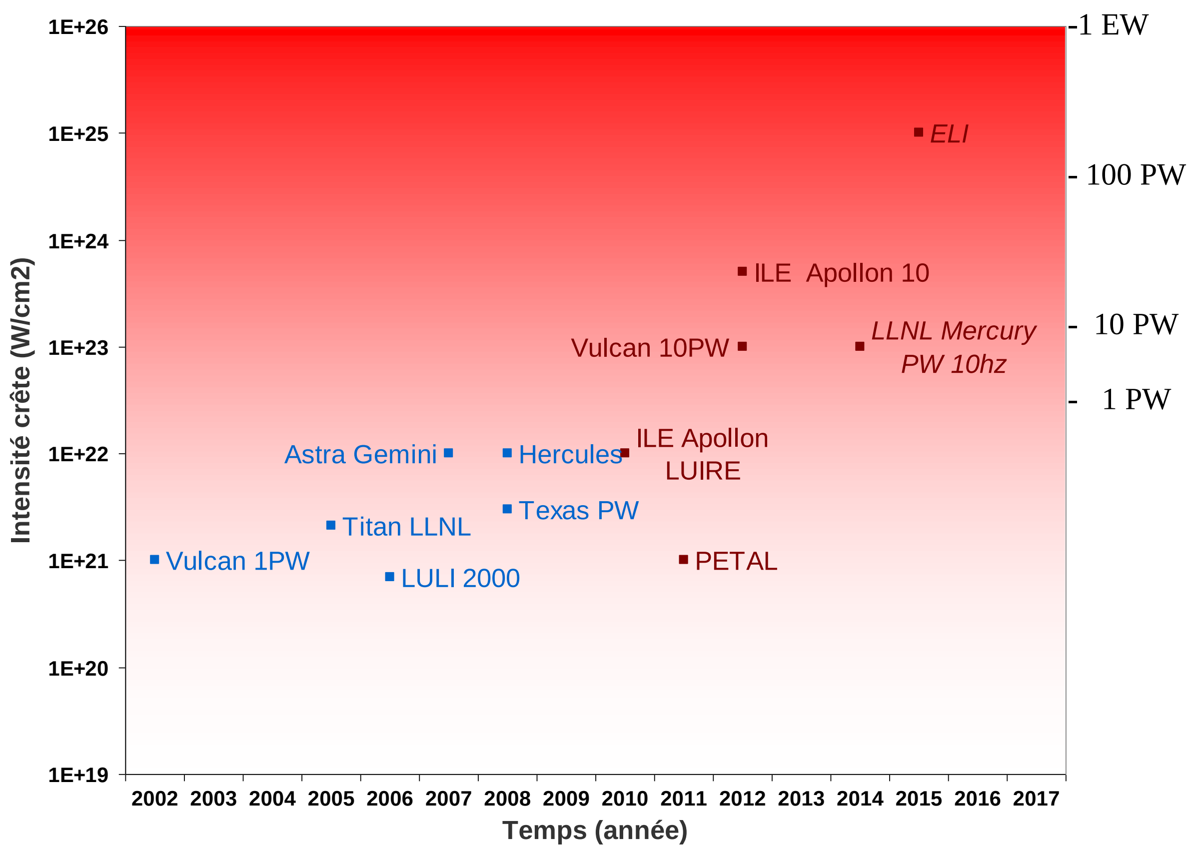
ABSTRACT

Small bubbles can be observed in both sapphire and Ti-sapphire bulk crystals grown by Czochralski technique (Cz). Various thickness of wafers cut from the grown ingots were studied by optical microscopy. Bubbles distribution has different regulation in sapphire and Ti-sapphire crystals. All bubbles are spherical and have a diameter range from 2 μm to 5 μm in sapphire crystals while 10–45 μm in Ti-doped sapphire crystals. Some adjacent bubbles congregated into defects present various sizes and shape. The bubbles density increases as a function of pulling rate and rotation rate. The effect of bubbles on optical characterizations of Ti-sapphire crystals has been studied.

Large TI-DOPED SAPPHIRES Ultrahigh Intensity laser



1E+26
1E+25
1E+24
1E+23
1E+22
1E+21
1E+20
1E+19
Intensité crête (W/cm2)
-1 EW
- 100 PW
- 10 PW
- 1 PW
ELI
ILE Apollon 10
Vulcan 10PW
LLNL Mercury PW 10hz
Astra Gemini
Hercules
ILE Apollon LUIRE
Texas PW
Titan LLNL
Vulcan 1PW
LULI 2000
PETAL
2002 2003 2004 2005 2006 2007 2008 2009 2010 2011 2012 2013 2014 2015 2016 2017
Temps (année)

Four generic approaches for 10 Petawatt

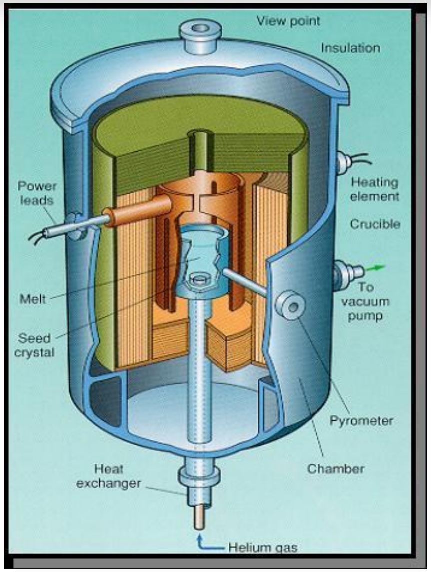
Gain material	Ti:Sa	OPCPA	Mixed Glass	Nd:Glass
Pump source	Nd:Glass 2ω	Nd:Glass 2ω	Flashlamp	Flashlamp
Pulse duration [fs]	15	30	150	500
Energy at target [J]	150	300	1500	5000
Beam quality ~ Strehl ratio				
Grating technology	Au – 1480 l/mm	Au – 900 l/mm	MLD – 1780 l/mm	MLD -1780 l/mm
TOTAL energy extraction (optical to optical)	13%	11%	78%	78%
1ω Energy required* [kJ]	1.05	2.4	1.86	6.2
Number of grating tiles required for final grating** (LLNL size gratings)	1	1	3	6

* assuming perfect beam profile
** excluding any safety factors

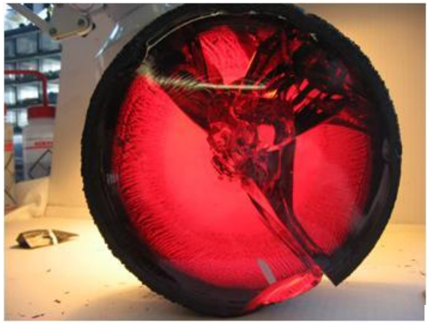
System cost is driven by two related issues:
Pump laser energy and final optics aperture

On way to produce large Ti: sapphire is the **Heat change method (HEM)**.

A 180mm diameter Ti: sapphire whose laser performance is considered acceptable was produce by this technique



However, the reproducibility of the process proves difficult. The HEM method produce lot of internal strain. The crystals have High possibility to produce cracks.



In Europe (France), we decided in 2009 to take up the challenge to develop sapphire crystal Ti laser quality.

In frame of national project Titansaphir (ILM, Simap, RSA le rubis, Cyberstar, Amplitude) we investigate the development and production of large Ti: sapphire for High Power Laser (P>1 PW)

Building on its expertise in the manufacture of doped titanium powders and doped sapphire crystallization in general, RSA was able to develop a reproducible process, crystallized by a specific method Kyropoulos.

Ingots 6 Kg and 100 mm in diameter with laser quality was demonstrated in 2012.

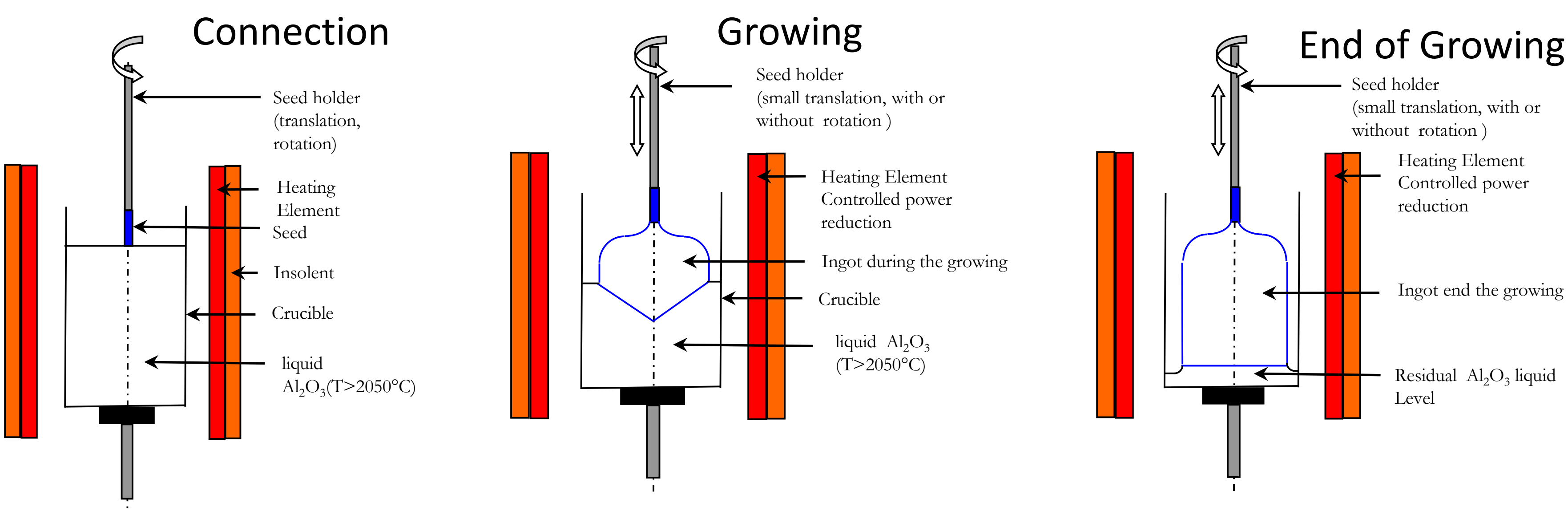
Ti: saphir: of 100mm/6kgs produce in RSA Le Rubis company

PHD thesis A. Nehari (2011) UCBL LYON1,

A. Nehari, A. Brenier, G. Panzer, K. Lebbou, J. Godfroy, S. Labor, H. Legal, G. Cheriaux, J.P .Chambaret, T. Duffar, R. Moncorgé, Crystal growth & design vol 11, (2011) 445-448

2: Large Ti-DOPED SAPPHIRES grown by Kyropoulos

3 phases



3: Spatial distribution of titanium

As the titanium (effective) segregation coefficient differs from unity ($K = Cs/Cl < 1$):

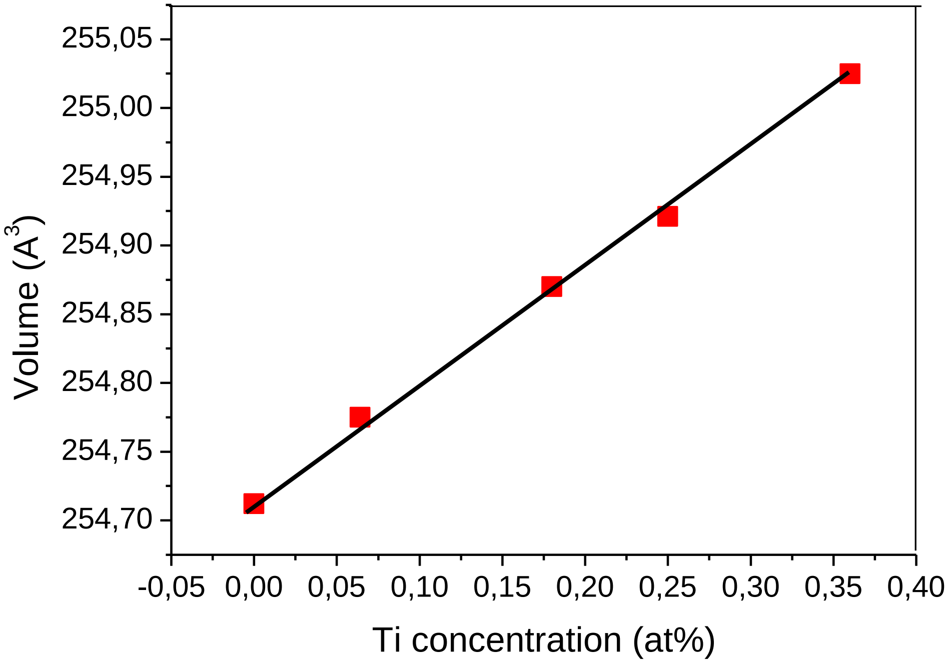
- a high proportion of (Ti^{3+}) active ions
- a good homogeneity in their spatial distribution

are key factors to obtain good quality $Ti:Al_2O_3$ laser crystals.

Ti-doped sapphire quantitative analysis

Crystals analysis
by ICP and GDMS

$C_s=kC_0(1-g)^{k-1}$ (k≈0.22)



Evolution of volume as a function of titanium concentration in Ti-doped Al_2O_3.Different fragment of crystals were cut from ingots and analysed by X-ray diffraction and ICP.

V=254.7141+0.8636[Ti]

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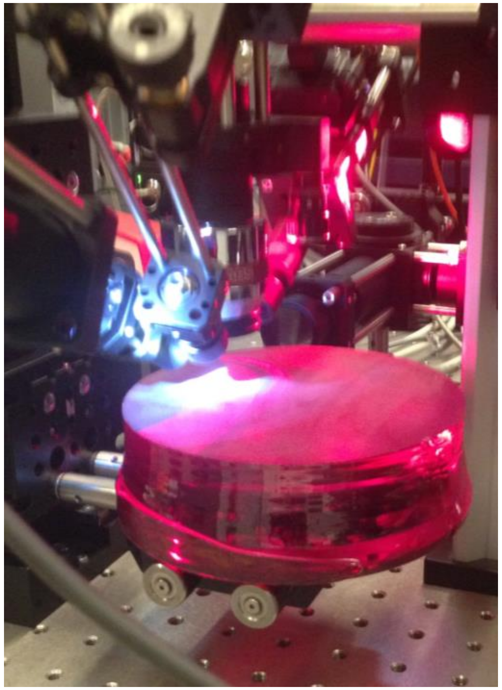
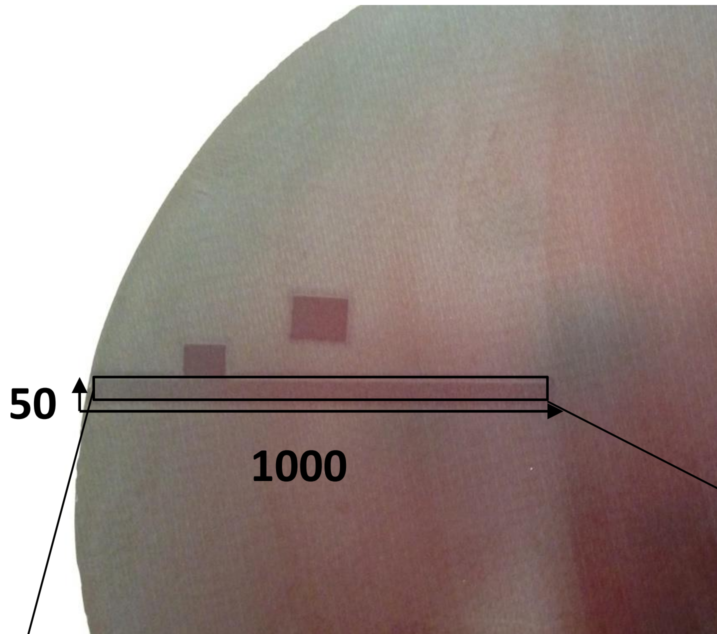
LIBS characterization to determine titanium distribution

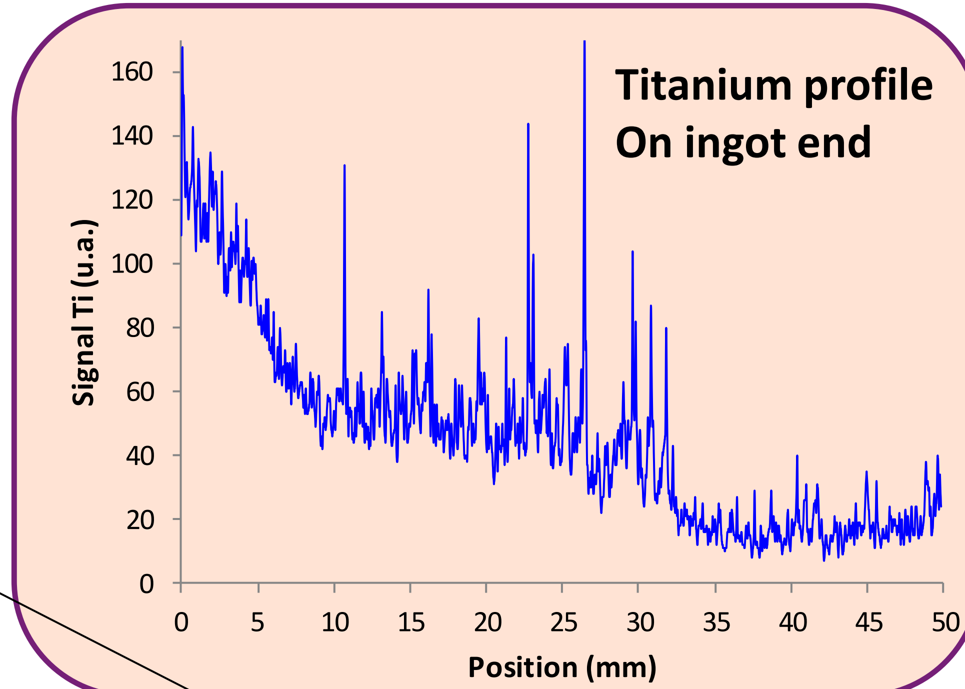


LIBS Instrument :

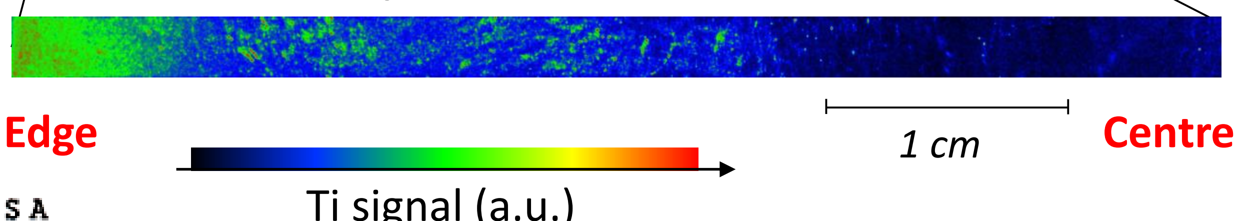
- Laser Nd:YAG 1064 nm (10 mJ at 10 Hz)
- Spectrometer : Czerny-Turner
- Detector : ICCD

- Titanium spectral rang (319 – 367 nm)
- 1000x50 Matrix, each measure is 50 microns spaced

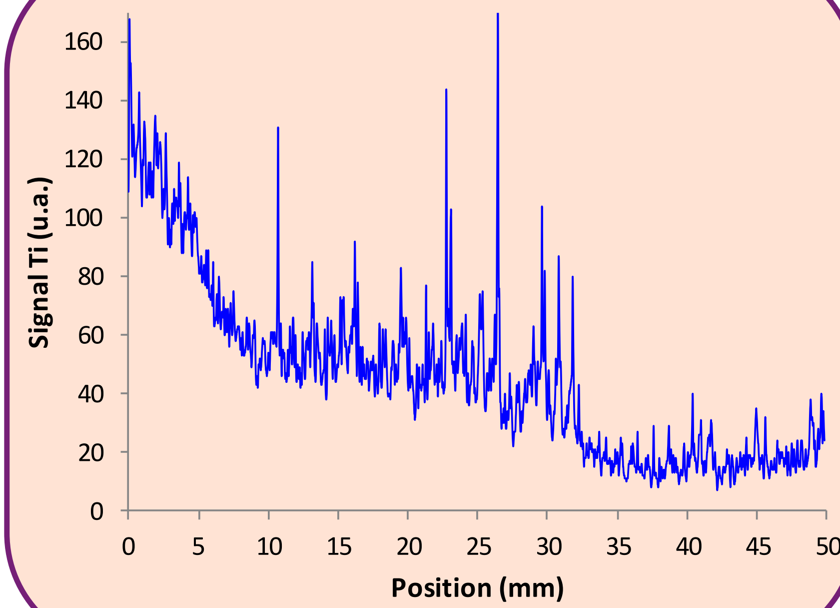




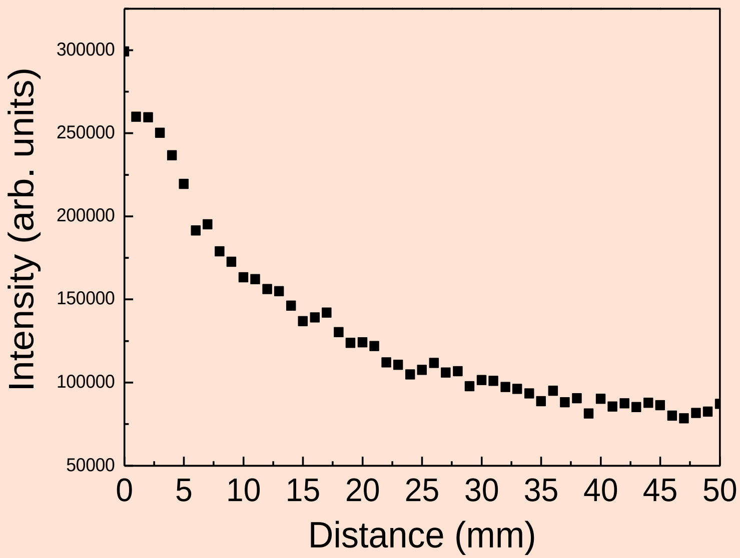
Map of the Titanium element



Titanium profile obtain by LIBS



Ti^{3+} profile obtain by luminescence



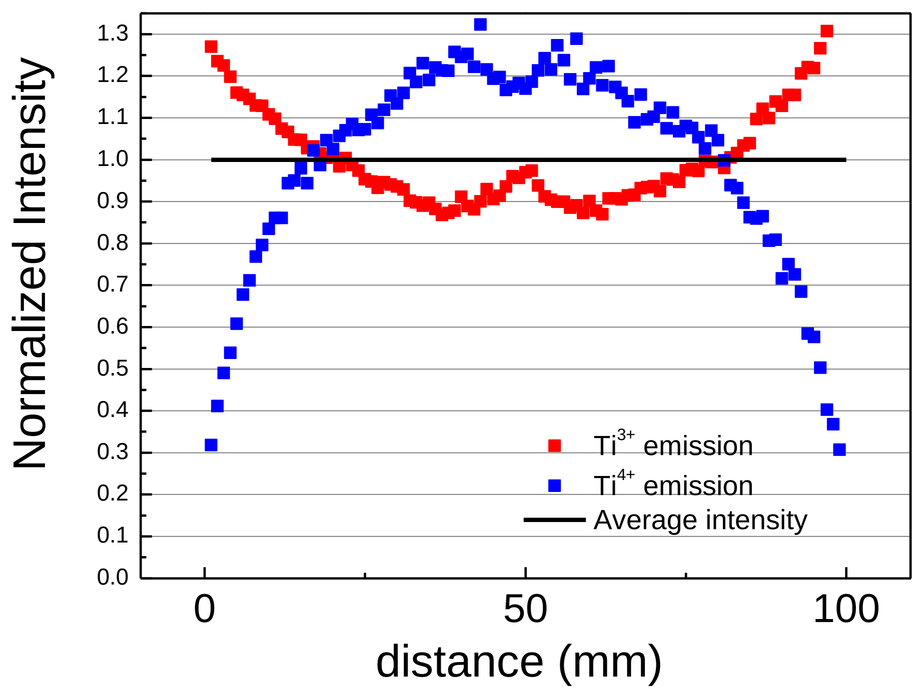
The two profile present a similar shape.
The LIBS profile is noisy by the surface roughness.

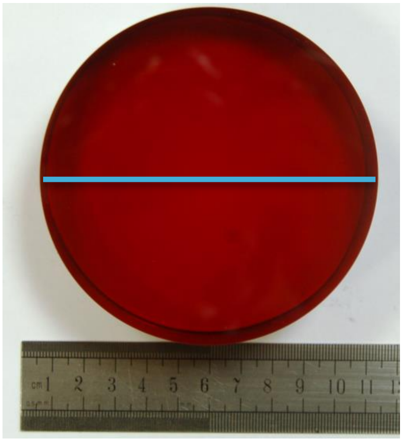
We need a series of reference samples with Ti concentration perfectly now to calibrated the LIBS measurements

Profiles of the luminescence intensity in 100 mm sapphire wafer.

The Ti^{3+} and Ti^{4+} distribution in the material can be evaluated by a measurement of the variation of luminescence intensity :

- at 730 nm after excitation at 532 nm for the Ti^{3+}
- at 420 nm after excitation at 256 nm for the Ti^{4+}





We successfully achieve a good homogeneity of the Ti^{3+} present in the diameter. But the variation of Ti^{4+} have to be controlled to obtain a high homogeneity in the FOM value in sample.

4 : Titanium valence states (evaluation of the FOM)

Ti: sapphire laser efficency are due to trivalent ion Ti^{3+} introduced into the crystal matrix; or Titanium may take different valence states (Ti^{3+}, Ti^{4+}).

The control of the Titanium valence states in the sapphire also a crucial factor.

Figure of Merit (FOM)

Ti^{4+} absorb the emitted laser energy and will reduce optical yield of the component; therefore is defined for Ti: sapphire a Figure of Merit (FOM) :

$$\text{FOM} = \frac{\alpha_{532\ nm}}{\alpha_{800\ nm}}$$

$\alpha_{532\ nm}$: absorption at the pump wavelength
$\alpha_{800\ nm}$: absorption at the emission wavelength

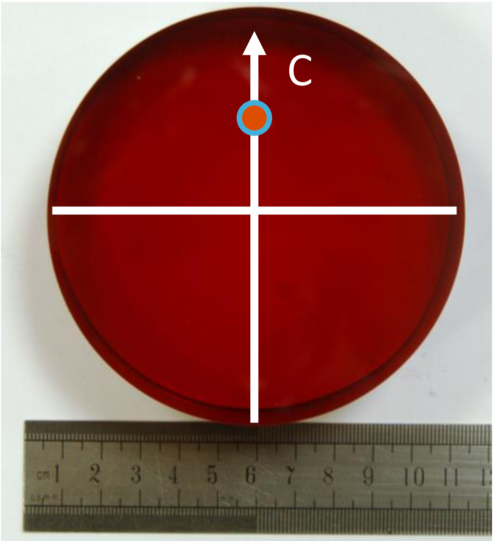
This FOM is correlated to ratio Ti^{3+} / Ti^{4+}, but also strongly depends on the geometry of the tested components.

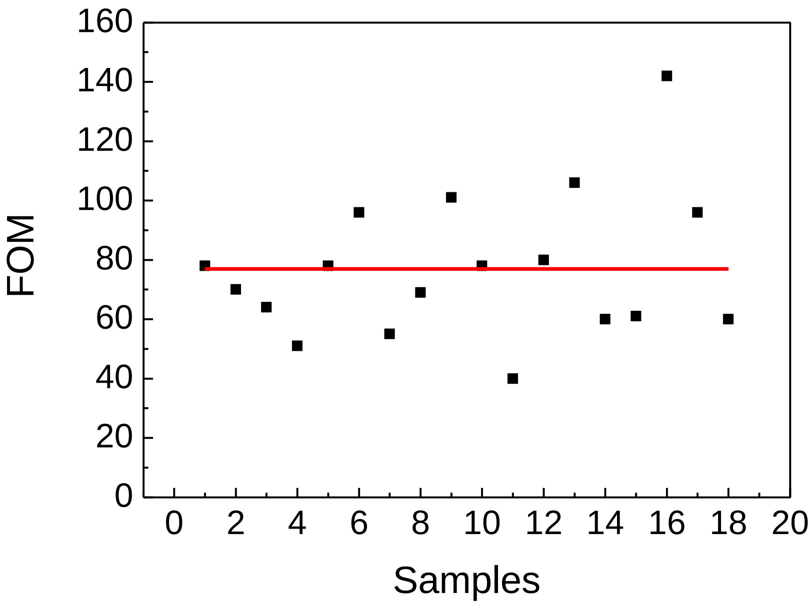
On **small components (<cm)** it is possible to obtain high values of **FOM (250) after annealing** in a reducing atmosphere;

On **post grow samples** it is more common to measure FOM 50 to 100.

FOM measured on the last series of 10 cm samples

$$FOM = \frac{\alpha_{532\ nm}}{\alpha_{800\ nm}}$$



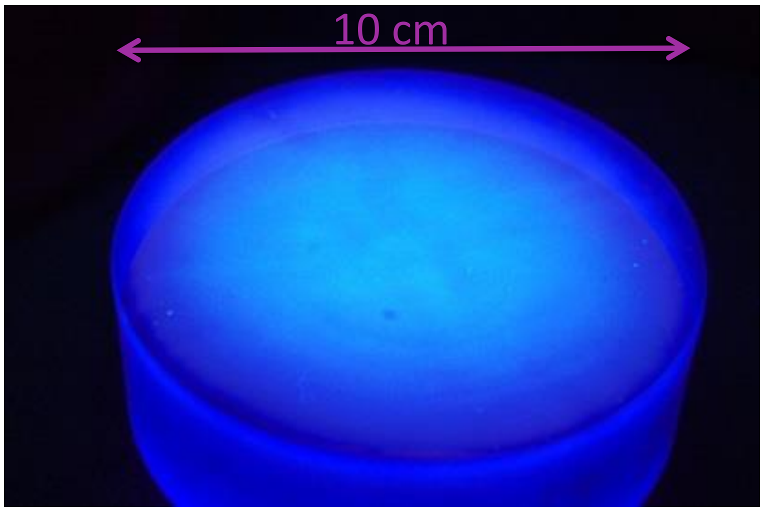


On the last 18 samples with 10 cm diameter, we obtain average FOM of 77.
A wafer corresponding to FOM 80 can be used as component for CPA.

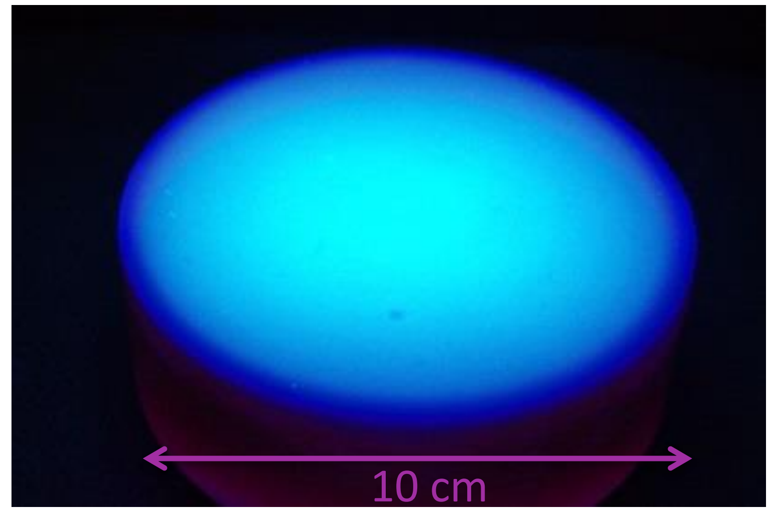
4 : Titanium valence states (evaluation of the FOM)

Picture of the Ti^{4+} luminescence observed on two 100 mm diameter Ti: sapphire sample upon UV lamp (256 nm) excitation.

Sample A

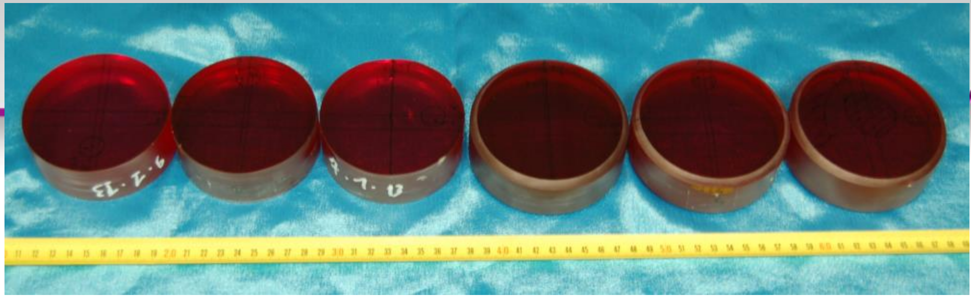


Sample B



Sample A present some inhomogeneity on the Ti^{4+} distribution.

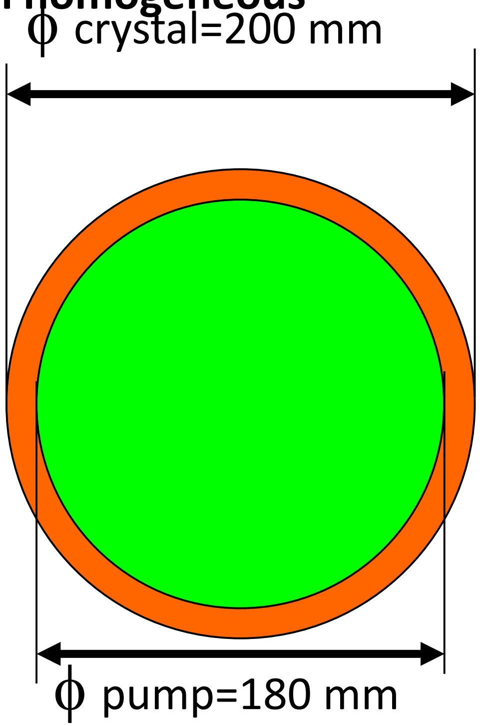
Sample B is much more homogenous but the amount of Ti^{4+} is to high.



We have succeeded to grow, large Ti-doped sapphire crystals by Kyroupolos technique, with diameter >100 mm and very soon >150 mm.

We obtain a good homogeneity in the radial distribution of the Ti^{3+} concentration in the sample.

Crystal quality improvement is still under progress to achieve high homogeneous material.
We need large crystal (extreme light)
300J after compression → 600 joules after amplification
(50% compression efficiency)



Crystal
Diameter: 200 mm
Thickness: 50 mm
Absorption (@527 nm): 94%

Injection
Energy: 50J
(Diameter (flat-top): 170.5 mm
Fluence: 210mj/cm^2

Pump:
Energy: 8 x 200 j
Diameter : (flat-top): 180mm
Amplification time: 30 ns
Fluence/ face: 3.5J/cm^2

Thank you for your attention