Gradually Doped and Large Diameter Yb\textsuperscript{3+} Doped YAG Crystals for High Power Solid State Laser Applications

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In 2008, LULI initiated research activities on crystal growth in collaboration with Laserayin Tekhnika, Yerevan, Armenia. The aim is to engineer laser gain media tailored to face the requirement imposed by developpement of HEC DPSSL laser systems through the world:

- **Thermal** and Amplified Spontaneous Emission (ASE) Management
- **Larger** size gain medium

Developing YAG crystals with variable Yb ion concentration appears as a solution of choice to homogenize the stored energy distribution within the gain medium. This is especially true in the context of Lucia amplifiers active mirror architecture.
Outline

• Impact of gradient doped gain medium on thermal and ASE management
• YAG growth techniques
• Yb:YAG growth with Bagdasarov method
• Simple model for gradient doping growth
• Doping measurement techniques
• Experimental results on gradient crystal growth
• Experimental campaigns aiming at improving our model
• Large Yb:YAG crystals
• Impact of gradient doped gain medium on thermal and ASE management

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Gain medium engineering

Constant doping
0.75 cm

Variable doping
0.75 cm

Yb$^{3+}$ doping [at.\%]

longitudinal position [cm]

Constant doping distribution
Variable doping distribution
Gradient doping sets gain below ASE oscillation threshold \((g_{0\text{max}}L<4)\)
Gradient doping impact on stored energy distribution ...and therefore on thermal management

- Constant doping: 0.75 cm
- Variable doping: 0.75 cm

Graph showing:
- Stored energy density [J/cm³]
- Longitudinal position [cm]

- Constant doping distribution
- Variable doping distribution
Impact on gain medium volume requirement

6 J/cm² stored energy in all cases

\[ g < 1 \Rightarrow \text{low ASE losses} \]

A

Constant doping
1.3 at%

1.15 cm

6.08 J/cm²

B

Variable doping
1.3 at%

0.75 cm

6.10 J/cm²

Such a 35% decrease on requested gain medium volume can have a dramatic impact on very large scale facility design trade....

What is the total weight of the 4320 homogeneously doped glass slabs required on LMJ facility ?...

125 tons
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Yttrium Aluminum Garnet has a cubic unit cell (yellow Yb ions replace some grey Y).

Cristallographic axis [100]
YAG phase diagram

YAG is obtained by stoichiometric mixing of 3 Yttria (Y$_2$O$_3$) and 5 Alumina (Al$_2$O$_3$): $3/(5+3) = 37.5\%$

\[ 5 \text{ Al}_2\text{O}_3 + 3 \text{ Y}_2\text{O}_3 \rightarrow 2 \text{ Y}_3\text{Al}_5\text{O}_{12} \]
The Czochralski technique is traditionally used for YAG growth. It is a well known technique where the grown crystal does not experience contact with the crucible. Drawbacks are:

- Cores and light scattering particles
- Large weight loss of iridium crucible
- Instability of solid-melt interface
YAG growth techniques: Bridgman

Starting material is loaded in a vertically moving crucible

- No possibility of in-situ observation

- Mechanical interaction between the crucible and the crystal

- Technical issues for extracting the grown crystal
YAG growth techniques: TGT

Starting material is loaded in a **static** crucible (ampoule shaped)
Heat distribution is vertically moving upwards

Drawbacks are the same as for Vertical Bridgman Technique

1 - crucible
2 - melt
3 - crystal
4 - heater spires
5 - thermal pinhole
6 - thermocouples
Bagdasarov technique

Bagdasarov technique (1964) is also known as:
**Horizontal** Bridgman Technique (HBT),
Horizontal Direct Crystallization (HDC),
Boat method in reference to the crucible shape,
Horizontal Direct Solidification (HDS)

The method is mainly used to produce high quality large size sapphire. It is also very effective to grow YAG crystals enriched with different dopant ions (Yb, Nd, Eu, Er, Ce...).
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Bagdasarrov technique

Starting material is loaded in a horizontally moving crucible

Molten phase (length = $L_m$)

Crystal phase

Seed

Starting material

Heater (Wo)

Crucible (Mo)

Empty crucible

Starting material loaded

Final boule
Bagdasarov furnace

Growth station

Crucible carrier

Crucible carrier with thermal shields
Bagdasarov furnace heater

1930°C temperature obtained with 22 Volts (1kA)

5 Tungsten spires heater
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Simple model for doping ion distribution

Initial starting material distribution

Yttria + Alumina

Yttria + Alumina + Yb Oxide

Top view

Side view

Yb Oxide concentration $C(x)$

Origin at crucible’s tail

$d$

$h$

$X$
Simple model for doping ion distribution

Relative motion between crucible and heat zone

Yb Oxide concentration $C(x)$

Heater tungsten spires

Melting zone $L_m$
Simple model for doping ion distribution

Yb starting (t=0) distribution in the crucible referential with origin at seed

Yb final distribution
Hypothesis
1. Segregation coefficient is considered equal to unity
2. Instantaneous Yb ions diffusion in the melt
3. Height h considered as constant over the process
4. $L_m$ constant

Differential distribution Concentration: 
\[ C(x + dx) = \frac{C(x)L_m - C(x)dx + Ndx}{L_m} \]

Concentration distribution: 
\[ C(x) = N \left( 1 - e^{-\frac{x}{L_m}} \right) \]
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Electron Probe Micro Analysis (EPMA)

EPMA provides quantitative and qualitative measurements of chemical composition at the micrometer scale in solid samples without destruction.

CAMECA SX 100 EPMA at the Laboratoire Magmas et Volcans

Inductively Coupled Plasma-Mass Spectrometry (ICP-MS)

1-Yb:YAG sample dissolved into liquid solution
2-solution is ionized with Inductively* Coupled Plasma (ICP)
3-Separation of the ions is performed with a Mass Spectrometer (MS)

* An inductively coupled plasma (ICP) is a type of plasma source in which the energy is supplied by electric currents which are produced by electromagnetic induction, that is, by time‐varying magnetic fields.
Yb concentration measurements: RBS

Rutherford Back Scattering (RBS)

RBS determines the composition of Yb:YAG samples by measuring the backscattering of a beam of high energy ions (here $X^+$) impinging the sample.

Yb:YAG RBS spectrum

Van de Graaff ion accelerator at the Institut des Nanosciences de Paris (INP)
## EPMA, ICP-MS and RBS comparison

<table>
<thead>
<tr>
<th>Doping growth reference</th>
<th>EPMA</th>
<th>ICP-MS</th>
<th>RBS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample A [at%]</td>
<td>2</td>
<td>2.01+/-0.1</td>
<td>1.9+/-0.04</td>
</tr>
</tbody>
</table>

- **Destructive and underestimating**
- **Large facility with access time constraints**

EPMA appears to be very accurate and easiest in use technique and has been chosen as a main technique.
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• Doping measurement techniques

• **Experimental results on gradient crystal growth**

• Experimental campaigns aiming at improving our model

• Large Yb:YAG crystals
Four growth sequences performed

Different shaped crystals are extracted, polished,... for further testing
Yb experimental concentration distribution

Yb concentration gradients up to ~3 at%/cm are obtained

Yb$^{3+}$ ions distribution within the gradient doped crystal
Fluorescence at 1030nm

Counter-gradient direction

Laser Source 940nm

Camera
Fluorescence at 1030nm

Gradient direction

Laser Source 940nm

Camera
Impact of gradient doping is clearly revealed
Thermal imaging: experimental setup

Laser 940nm 80W

Water cooled Copper plates

Gradient doped crystal

Camera
A more than 15 degrees difference is observed for opposite gradient directions.

Higher gradient will be required to reach an even more homogeneous $T^\circ$ distribution.
Our simple model does not allow to understand the gradient value experimentally observed.

Molten zone length $L_m$ were considered as constant during the growth process.

$\Rightarrow$ Experiments were set up to evaluate $L_m(x)$ and $T(t,x)$.
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**Simple model for doping ion distribution**

**Hypothesis**
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**Differential distribution Concentration:**

\[
C(x + dx) = \frac{C(x)L_m - C(x)dx + Ndx}{L_m}
\]

**Concentration distribution:**

\[
C(x) = N(1 - e^{-\frac{x}{L_m}})
\]
Molten zone $L_m$ shrink experiment: 1st step

Molten zone shrinks in size within the growth process. Quantifying this shrinkage will allow avoiding constant molten zone length approximation and lead to better matching with experimentally observed gradients.

No translation of the crucible!!!

Resulting boule $L_m \approx 11$ cm

Heating sequence

thermal shields
Molten zone $L_m$ shrink experiment: 1\textsuperscript{st} step

In step 2, the crucible (still loaded with resulting content of step 1) will now move slowly inside the heat zone (~1.5 mm/h)

Translation occurs with a 1.5mm/h rate like during standard growth.

![Diagram showing starting and final position of the crucible carrier with a graph indicating the initial voltage start.](image-url)
The molten zone in the beginning of the process was almost 110 mm.

By the end of the process, the molten zone is almost twice less in length, i.e. ~50 mm.
**Molten zone $L_m$ shrink experiment: 2nd step**

Explanation lies in the fact that the grown crystalline part exhibits higher thermal conductivity and therefore evacuates the heat very effectively.

Molten length new expression can be linearly approximated by:

$$L(x) = L_m(0) + x \frac{L_m(\text{final}) - L_m(0)}{D}$$

Where $D$ is a total translation.
Temperature distribution evolution experiment

Besides the molten zone length $L_m$ reduction during the growth process, the temperature distribution within the crucible evolves as well.

Three C type thermocouples are attached to the crucible via the Mo holder in appropriate positions and are electrically insulated from the crucible.
Temperature distribution evolution experiment

Filling the crucible with starting material

....inserting the crucible in the furnace...

...and monitoring the temperatures with the 3 thermocouples
1st experiment

Observed Temperature distribution

Input boule

Resulting boule

Results:

\[ T_{1\text{max}} = 2062°C \]
\[ T_{2\text{max}} = 1869°C \]
\[ T_{3\text{max}} = 1344°C \]

\[ T_{1\text{max}} - T_{2\text{max}} = 193°C \]
\[ T_{2\text{max}} - T_{3\text{max}} = 525°C \]
The temperature in the melt, starting material and crystallized solid is measured for different positions of the crystals. We observe different temperature distributions.

These results can be used to evaluate effective thermal conductivity for the different phases.

The results are also very important in order to grow composite crystals.

Further analysis and experiments are needed to evaluate the temperature fields in all axes to get full control over this parameter.
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• Large Yb:YAG crystals
The crucibles for large YAG crystals

Larger crucibles were fabricated
The large YAG crystals

92mm Ce:Yb:YAG crystal

60mm Yb:YAG crystal currently used in LUCIA main amplifier
Absorption spectra

Absorption band of HDC-grown 0.4 at.%-doped Yb:YAG Large Crystal

Characteristic Yb:YAG absorption lines spectra is observed. Also Ce trivalent ions absorption is detected.
**Doping homogeneity**

Absorption

- 0.41 +/- 0.02 at% of Yb$^{3+}$

Typical Yb$^{3+}$ absorption spectra is observed

Typical Ce$^{3+}$ absorption bands are observed
X-Ray (Cu-a) Topograms reveal no grains

Constant 2 at% doping level / 60 mm diameter crystal used for Lucia amplifier

Thanks to Joachim Hein, IOQ, FSU, Jena, Germany ......
Depolarization in the crystals

Stresses are concentrated mainly near the periphery, which is also the area of interaction of the crystal and molybdenum crucible.
Outlook

Variable doping

• Increasing the values for doping gradients through in-growth control of melt composition
• obtaining variable doping “hill” or “step” shape profiles
• growing gradient doped crystals with different dopants

Large crystals

• tailoring the furnace in order to increase the diameter of growing crystals
• growing large crystals of other garnets (for example `LuAG`)

Method characterization

• Further experiments on growth characterization in order to improve the model
THANK YOU FOR ATTENTION
GAIN THANK YOU FOR ATTENTION
### Gradient doped Yb:YAG crystals

<table>
<thead>
<tr>
<th>Author(s)</th>
<th>Title</th>
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<tbody>
<tr>
<td>R. Triboulet</td>
<td>The travelling heater method (THM) for Hg(1-x)Cd(x)TE and related materials</td>
</tr>
<tr>
<td>Denis Freiburg and etc.</td>
<td>Power scaling of Diode End-Pumped Nd:YAG Lasers by Hyperbolic Dopant Concentration Profiles</td>
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<tr>
<td>Ralf Wilhelm and etc.</td>
<td>Power Scaling of End-Pumped Solid-State Rod Lasers by Longitudinal Dopant Concentration Gradients</td>
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<tr>
<td>Xiaodong Xu</td>
<td>Comparison of Yb:YAG crystals grown by Cz and TGT method</td>
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<tr>
<td>Our journal of crystal growth</td>
<td></td>
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<td>Our Optical materials express</td>
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</tbody>
</table>
Horizontal Direct Crystallization (HDC) experimental set-up

- Crucible carrier with thermal shields
- Mo Crucible
- Observation window
- Furnace
- Growth station
How it is calculated!

\[
\begin{align*}
\frac{d\beta}{dt} &= \left\{ \sigma_{\text{abs}P} - \left( \sigma_{\text{em}P} + \sigma_{\text{abs}P} \right) \beta \right\} \frac{I_P}{h \nu_P} - \frac{\beta}{\tau_{\text{fluo}}} \\
\frac{dI_P}{dz} &= N_{\text{tot}} \left\{ \left( \sigma_{\text{em}P} + \sigma_{\text{abs}P} \right) \beta - \sigma_{\text{abs}P} \right\} I_P
\end{align*}
\]
ASE losses impact on gain

When the pump intensity exceeds 11 kW/cm², lateral losses cannot compensate for single path ASE oscillation regime depleting the gain.

Taking advantage of full pumping brightness now possible with adequate cladding.
Temporal evolution of single pass gain during and after a 1 ms single pumping shot.
LUCIA System: Active mirror concept

LUCIA amplifying stages rely on active mirror architecture

Diode pump

Pump and input extraction beams are reflected at the back surface of the disk

Crystal or ceramic

Pump beam at 941 nm

Incident beam

Reflected beam

at 1030 nm
Gradient doped crystals: Numerous positive impacts

Thermal Management

Amplified Spontaneous Emission Management

Gain distribution

Positive Impacts

125 tons

Gain medium volume requirement

Stored Energy Distribution
• Laser materials for LUCIA system: Yb:YAG
• Gradient doped materials and large crystals
• Yb:YAG growth with Bagdasarov method
• Doping verification different methods
• Gradient crystal growth
• Results on gradient crystals
• Large Yb:YAG crystals
• Other YAG crystals grown by Bagdasarov method
• Laser materials for LUCIA system: Yb:YAG
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  • Other YAG crystals grown by Bagdasarov method
• Simple energy level system
• Long fluorescence lifetime (about 1ms)
• Suitability to high performance InGaAs/GaAs diode pumps
• No upconversion, cross relaxation and excited-state absorption

Energy levels of Yb and Nd ions. Typical laser transition lines are represented for both pump absorption and laser emission.

* Sébastien Chénais et al., Progress in Quantum Electronics 30 (2006) 89
• Laser materials for LUCIA system: Yb:YAG

• Gradient doped materials and large crystals

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The ASE Multiplier is a figure of merit quantifying ASE losses. It can be seen as a lifetime reducer.

\[ \tau_{\text{eff}} \propto \frac{\tau}{M_{\text{ASE}}} \]
Bagdasarov technique: growth conditions

- Crystallization atmosphere: *vacuum*, recovering, neutral
- Crucible material: *molybdenum* etc...

- Thermal shields: *tungsten and molybdenum*, graphite etc...

- Heater: tungsten

- Growth rates: 1-10mm/hour
Bagdasarov technique: growth steps

1-Powder weighting with appropriate mass ratio of Yb2O3 (or other dopant), Y2O3 and Al2O3 and placing it in special crucible

2-Melting the content by translating powder loaded crucible through heat zone under vacuum

3-Extracting the solid solution, preparing crackle

4-loading it into seeded boat-shaped crucible
**Bagdasarov technique: growth steps**

5-Placing the crucible in the furnace (with seed partially out of heat zone), pumping the vacuum, then rising the voltage on the heater. As soon as the zone under heater is molten translation starts.

5-Mechanically extracting the boule by destroying the crucible
Characterization of the heater temperature

Tungsten-Rhenium thermocouple with open head and protected by ceramic substrates in order to attach to the heater.

Straight vertical lines defines the limits of the areas with constant voltage.

Temperature evolution of the heater

![Graph showing temperature evolution over time with voltage levels at 5V, 15V, and 19V.](image)
Impact on thermal management: Cooling scheme

- **Air Cooling**
  - Temperature: 295 K
  - Heat Transfer: 10 W/m².K
- **Water Cooling**
  - Temperature: 288 K
  - Heat Transfer: 15000 W/m².K

Pumping-cooling sketch used in our model and calculation parameters.
Impact on thermal management

Axial temperature distribution evolution over 1min at 10hz

1.3 at % Constant doping level
1.15cm crystal: Max temp. is **383** K and continues rising after 1min at 10 Hz operation

1.9 at % Constant doping level
0.75cm crystal: Max temp. is **357** K after 1min at 10 Hz operation

Variable 1.3-2.3 at % doping level
0.75cm crystal: Max temp. is **349** K with thermal equilibrium after 1 min at 10 Hz
Besides experiencing much less ASE losses the gradient doped crystal also exhibit a slightly better thermal distribution.
YAG growth techniques: Bridgman and Stockbarger

Starting material is loaded in a vertically moving crucible

- No possibility of in-situ observation
- Mechanical interaction between the crucible and the crystal
- Technical issues for extracting the grown crystal
**Yb concentration measurements : EDX**

**Energy Dispersive X-ray spectroscopy (EDX)**

1. A high-energy electron beam is focused into the sample to stimulate the emission of characteristic X-rays from YAG
2. The composition of the specimen can be retrieved

---

EDX apparatus used for our sample at HTSC, Armenia
2nd experiment

Input boule = 1st experiment

Observed temperature distribution

Results:
\[ T_{1\text{max}} = 1887^\circ C \]
\[ T_{2\text{max}} = 1989^\circ C \]
\[ T_{3\text{max}} = 1921^\circ C \]
\[ T_{1\text{max}} - T_{2\text{max}} = -102^\circ C \]
\[ T_{2\text{max}} - T_{3\text{max}} = 78^\circ C \]
3rd experiment

Conclusion:
\[ T_{1\text{max}} = 1495^\circ C \]
\[ T_{2\text{max}} = 1696^\circ C \]
\[ T_{3\text{max}} = 1930^\circ C \]
\[ T_{4\text{max}} = 1980^\circ C \]
\[ T_{1\text{max}} - T_{2\text{max}} = -201^\circ C \]
\[ T_{2\text{max}} - T_{3\text{max}} = -234^\circ C \]
\[ T_{4\text{max}} - T_{3\text{max}} = 60^\circ C \]
Doping level measurement for the 90mm crystal

<table>
<thead>
<tr>
<th>Energy-Dispersive X-Ray Analysis</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.39±0.17 at% of Yb</td>
</tr>
<tr>
<td>No Ce$^{3+}$ detected</td>
</tr>
</tbody>
</table>

Line Spectrum(1)
Depolarization in the crystals

Stresses are concentrated mainly near the periphery, which is also the area of interaction of the crystal and molybdenum crucible.
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Defects in the crystals

- A few inclusions are detected near the interface of boule and container with microscope analysis

- no bubbles were detected

- The final product crystal was cut in the part not influenced by this defects