Transparent Polycrystalline Materials: Historical Developments and Next Generation Applications

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Optoelectronics Management Network
CREOL Industrial Affiliates Symposium
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Outline

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- Ceramic vs. Single Crystal
- Nanopowder Characterization
- Mechanical Characterization
- Laser Test Results
- Future Directions
- Conclusions
Acknowledgements

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Motivation

• Historical perspective of solid-state laser development
• Transition from pulsed to the continuous lasing regime
• Limitations of thermal loading and optical damage
• Glass versus crystal media
• Limits to crystal growth techniques
• New host materials and new laser materials
• Dopant engineering
• New EO and active media
Historical Perspective

Historically, the first lasers were crystals - Thermal loading limits output energies and damage
Crystalline and Glass Laser Materials
Nd:YAG Single Crystal

Nd:YAG single crystal is grown by Czochralski method

- very slow growth rate (2-3 weeks)
- defect region exists
- need high temperature furnace
- need expensive Iridium crucible
- limited Nd doping range (1.4 at% max) as a result of concentration gradient

\[ \text{Nd}_{3x}Y_{3-3x}\text{Al}_{5}\text{O}_{12} \]

- cubic structure (Garnet)
- Nd replaces Y lattice
- ionic radius of Nd is larger than Y (\(\text{Nd}^{3+} : 0.098 \text{ nm}, \text{Y}^{3+} : 0.090 \text{ nm}\))

only 25% of melt can be used

(Ref. Yttrium Aluminum Garnet Laser Materials, VLOC brochure)
Wavefront Distortion is an Issue
Laser Glass Technology was developed for LLNL High Power Applications – Low rep rate, Low efficiency
Enter the ‘90’s – the age of diode pumping

808 nm pump for Nd:YAG …

…940 nm pump for Yb:YAG even better

\[ \text{Quantum Defect} (q) = h\nu_{\text{pump}} - h\nu_{\text{laser}} = h\nu_{\text{pump}} \left\{ 1 - \left(\frac{\lambda_{\text{pump}}}{\lambda_{\text{laser}}}\right) \right\} \]

With diode pumping, efficiencies increased from < 0.1% to > 30% and powers increased from 100W to > 100kW
Why Ceramic Gain Materials?
Definition of Ceramic

A polycrystalline, rigid body that consists of an ionic material that is manufactured from powders through a variety of consolidation and sintering processes that does not require a macroscopic (bulk) phase change of the material to achieve final density.

Translucent (left) and transparent (right) Al₂O₃ (Apetz et al. J. Am. Ceram. Soc., 2003)

PLZT sintered at 1200°C a) whole specimen b) outlayer (Choi et al. J. Am. Ceram. Soc. 2001)
Milestones on the ceramic laser road

First ceramic laser materials (CaF$_2$)

Active research on Nd:Yttralox ceramic lasers

First CW ceramic Nd:YAG laser

CW ceramic Nd:YAG laser with 1.46 kW power and 50% efficiency

Modelocked Nd:YSAG ceramic laser

CW oscillation from Lu$_2$O$_3$, Sc$_2$O$_3$, and Y$_2$O$_3$ ceramic hosts doped by Nd$^{3+}$ or Yb$^{3+}$
Birefringence Prevents Transparency

- Birefringent materials: alumina, YVO$_4$, YLF, etc.
- Grains Randomly Oriented in Polycrystal
- Index of Refraction, $n$, changes upon crossing grain boundary
- Snell’s Law dictates deviation of light

- Toward normal if $n_1 < n_2$
- Away from normal if $n_1 > n_2$

- Birefringent ceramics will always be TRANSLUCENT
  - Degree of translucency, though, may be very good
Processing Challenge:

No Pores & Clean Grain Boundaries

Micrographs of Konoshima ceramic YAG (from website)
Transparency Requires Extremely Good Processing


Transparency Cannot Tolerate Pores & Inclusions!
## Transparent Polycrystalline Ceramic Materials

Ceramics with cubic structure are transparent

<table>
<thead>
<tr>
<th>Material</th>
<th>Composition</th>
<th>Crystal Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Yttrium Aluminum Garnet</td>
<td>$3Y_2O_3 \cdot 5Al_2O_3$</td>
<td>cubic</td>
</tr>
<tr>
<td>Yttria</td>
<td>$Y_2O_3$</td>
<td>cubic</td>
</tr>
<tr>
<td>Scandium oxide</td>
<td>$Sc_2O_3$</td>
<td>cubic</td>
</tr>
<tr>
<td>Lutetium oxide</td>
<td>$Lu_2O_3$</td>
<td>cubic</td>
</tr>
<tr>
<td>AlON</td>
<td>AlON</td>
<td>cubic</td>
</tr>
<tr>
<td>Spinel</td>
<td>$MgO \cdot Al_2O_3$</td>
<td>cubic</td>
</tr>
<tr>
<td>Zinc sulfide</td>
<td>ZnS</td>
<td>cubic</td>
</tr>
<tr>
<td>Alumina (Lucalox)</td>
<td>$Al_2O_3$</td>
<td>rhombohedral</td>
</tr>
</tbody>
</table>

Transparent Nd:YAG Polycrystalline Ceramics

Transparent components of sintered corundum with sub-μm microstructure
Nd:YAG ceramic polycrystal is processed by conventional sintering

- relatively short processing cycle (1 day)
- does not need Ir crucible for melting
- homogeneous composition
- defect region (facet or core) does not exist
- high Nd doping range (up to 9 at %)

- First attempted in 1984 by de With et al., but they produced translucent YAG.
- Udea, Yanagitani et al. reported laser generation in 2002.
Nd:YAG Manufacturing Process

<table>
<thead>
<tr>
<th></th>
<th>Single Crystal Growth</th>
<th>Ceramic Manufacturing</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Max temperature</strong></td>
<td>&gt;1970°C</td>
<td>&lt;1800°C</td>
</tr>
<tr>
<td><strong>Time at T_{max}</strong></td>
<td>~40 days</td>
<td>&lt;2 days</td>
</tr>
<tr>
<td><strong>Max rod φ</strong></td>
<td>35mm</td>
<td>15mm</td>
</tr>
<tr>
<td><strong>Max slab dimensions</strong></td>
<td>50mm x 200mm x 15mm</td>
<td>300mm x 300mm x 15mm</td>
</tr>
<tr>
<td><strong>Doping variation</strong></td>
<td>1.0% to 1.3%</td>
<td>None</td>
</tr>
<tr>
<td><strong>Maximum doping</strong></td>
<td>1.5%</td>
<td>9%</td>
</tr>
</tbody>
</table>
Polycrystalline Ceramic YAG Process - History

Co-precipitation

<table>
<thead>
<tr>
<th>Company</th>
<th>Konoshima</th>
</tr>
</thead>
<tbody>
<tr>
<td>Powder</td>
<td>Coprecipitate metal chloride</td>
</tr>
<tr>
<td></td>
<td>- complex process</td>
</tr>
<tr>
<td></td>
<td>- difficult to scale up</td>
</tr>
</tbody>
</table>

1200-1300°C
Slip casting
Vacuum in metal furnace
< 5 µm
1.46 KW

Reactive sintering

<table>
<thead>
<tr>
<th>World Lab Co.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oxide powder from alkoxide</td>
</tr>
<tr>
<td>- easy process</td>
</tr>
<tr>
<td>- economically competitive</td>
</tr>
</tbody>
</table>

Not necessary
Dry pressing (spray dried powder)
Vacuum in metal furnace
20-30 µm
700 Watt

Konoshima, 8 at% Nd:YAG

Ikesue 1.1 at% Nd:YAG

First Conference on Advances in Optical Materials; October 12, 2005
Nanopowder Synthesis

Liquid Flame Spray Pyrolysis (L-FSP)

Metal Organic Precursors:
Y, Nd, Al organic compounds in an alcohol/organic acid solvent
Facilities for Making Transparent Ceramics

Step 1: Prepare high purity powder
Step 2: Hot press powder
Step 3: Hot isostatically press (HIP) to clear transparency

Utilizes a simple and inexpensive process
Why Nano-Powders?

- Sintering driven by surface free energy
  - Specific surface area increases as particle size decreases
  - Surface energy increases as particle size decreases (Kelvin Eqn)
  - Sintering force increases as particle size decreases

0.01 to 0.1 mm powders achieve high density at lower temperature

Fig. 1: Open pore porosity of titania pellets vs. sintering temperature.

Porosity of Titania Films on Alumina

Kailash C. Jain
Delphi Research Labs, 51786 Shelby Parkway, Shelby Township MI 48315

Abs. 666, 204th Meeting, © 2003 The Electrochemical Society, Inc.
Ceramic Advantages

• Consolidation
  • Tape casting
  • Slip casting
  • Powder pressing
  • Near net shape fabrication – minimal waste from melt & kerf
  • High volume processes – use same technology as advanced ceramics
  • Functionally graded materials possible

• Sintering
  • Surface area reduction & densification at $T = \frac{1}{2}$ to $\frac{3}{4}$ of $T_{\text{melt}}$
  • No phase change & no constitutional supercooling
  • Microscopic mass transport distances & flat (0) furnace gradients
  • Lower temperature results in feasibility of new materials
Scaled Up Spinel to Large Sizes

1” diameter

5” diameter

1.8 km horizontal path at sea level with 40% relative humidity

12” x 16” window


Demonstrated 6 ppm/cm absorption loss at 1.06 µm

Many applications
NRL Spinel (MgAl$_2$O$_4$)

12” x 16” window
- Superior mechanical properties compared to CLEARTRAN° (ZnS):
  - 10x higher hardness
  - 2x higher fracture toughness
  - 3x higher strength
- High transmission 0.2-5.5 μm
  - Better than sapphire and ALON

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Spinel</th>
<th>CLEARTRAN°</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crystal Structure</td>
<td>Cubic</td>
<td>Cubic</td>
</tr>
<tr>
<td>Density (g/cm$^2$)</td>
<td>3.6</td>
<td>4.1</td>
</tr>
<tr>
<td>Hardness (kg/mm$^2$)</td>
<td>1645</td>
<td>150</td>
</tr>
<tr>
<td>Fracture Toughness (MPa.m$^{-1/2}$)</td>
<td>1.9</td>
<td>1</td>
</tr>
<tr>
<td>Refractive Index</td>
<td>1.72</td>
<td>2.25</td>
</tr>
<tr>
<td>Strength (MPa)</td>
<td>350</td>
<td>100</td>
</tr>
</tbody>
</table>

Jas Sanghera  PACRIM 2011 Symp 20 Mon. Jul 11,

Transparent Spinel is an excellent candidate for Vis-IR windows
ALON - Aluminum oxynitride

Conventional Glass Laminate

ALON® Laminates

Reconnaissance Window

50 cal AP

ALON® Hyper-Hemisphere for Counter-Manpads
# Sesquioxide Characterization

## Characterization of Yb-doped Single Crystal Oxides

<table>
<thead>
<tr>
<th>Property</th>
<th>YAG</th>
<th>Y$_2$O$_3$</th>
<th>Lu$_2$O$_3$</th>
<th>Sc$_2$O$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\lambda_{\text{laser}}$ (nm)</td>
<td>1030</td>
<td>1031</td>
<td>1032</td>
<td>1041</td>
</tr>
<tr>
<td>$\sigma_{\text{emission}}$ ($10^{-21} \text{ cm}^2$)</td>
<td>19</td>
<td>10.6</td>
<td>12.8</td>
<td>14.4</td>
</tr>
<tr>
<td>$\sigma_{\text{reabsorp}}$ ($10^{-21} \text{ cm}^2$)</td>
<td>1.2</td>
<td>0.8</td>
<td>0.7</td>
<td>0.7</td>
</tr>
<tr>
<td>$\Delta \lambda$ (nm)</td>
<td>8.5</td>
<td>14.5</td>
<td>13</td>
<td>11.6</td>
</tr>
<tr>
<td>$^2F_{5/2}$ lifetime ($\mu$s)</td>
<td>950</td>
<td>850</td>
<td>820</td>
<td>800</td>
</tr>
<tr>
<td>$^2F_{7/2}$ splitting ($\text{cm}^{-1}$)</td>
<td>785</td>
<td>874</td>
<td>903</td>
<td>1017</td>
</tr>
<tr>
<td>$\kappa$ ($\text{W m}^{-1} \text{K}^{-1}$)</td>
<td>11</td>
<td>$\geq$ 13.6</td>
<td>$\geq$ 12.5</td>
<td>$\geq$ 16.5</td>
</tr>
</tbody>
</table>

Advantages of Sc$_2$O$_3$ Host Material

## Highest Thermal Conductivity of Sesquioxide Hosts

<table>
<thead>
<tr>
<th>Material</th>
<th>Thermal Conductivity (W/mK)</th>
<th>Melting Point (°C)</th>
<th>Ion to Be Replaced</th>
</tr>
</thead>
<tbody>
<tr>
<td>Y$_2$O$_3$</td>
<td>14</td>
<td>2439</td>
<td>Y$^{3+}$ (0.892 nm)</td>
</tr>
<tr>
<td>Sc$_2$O$_3$</td>
<td>17</td>
<td>2485</td>
<td>Sc$^{3+}$ (0.750 nm)</td>
</tr>
<tr>
<td>Lu$_2$O$_3$</td>
<td>13</td>
<td>2490</td>
<td>Lu$^{3+}$ (0.848 nm)</td>
</tr>
<tr>
<td>YAG</td>
<td>11</td>
<td>1970</td>
<td>Y$^{3+}$ (0.892 nm)</td>
</tr>
</tbody>
</table>

(Ref: O. Casagrande et al. Evaluation of pulsed diode end-pumped Ytterbium doped sesquioxides: Comparison of Sc$_2$O$_3$, Y$_2$O$_3$ and Lu$_2$O$_3$)

### Readily Doped with Yb

Similar ionic radii of Sc & Yb allows ready substitution of Yb$^{3+}$ into Sc$^{3+}$ lattice sites.

(Ref: http://environmentalchemistry.com/yogi/periodic/ionicradius.html)
First demonstration of lasing using hot pressed ceramics:

- 2%-Yb:Y$_2$O$_3$
- 10%-Yb:Lu$_2$O$_3$
Er:Y$_2$O$_3$ transparent ceramics
Ceramic Development at Nanyang Technological University, Singapore

NTU-made YAG ceramics with different RE$^{3+}$ dopants

Full ceramic development process at Nanyang Technological University, Singapore (NTU)
Parts Processed at II-VI Inc.

- Very good optical quality achieved, lasing demonstrated, large parts fabricated.
Ceramic Nd:YAG – large sizes
- bonded materials
45 kW ceramic Nd:YAG LLNL laser

Solid State Heat Capacity Laser at Lawrence Livermore National Lab
SSHCL Cutting Capability

Cutting through 2.5 cm thick steel in 7 seconds.
Applications
Applications

• Defense
• Scintillators
• Smart Gear
• Engineered Materials
New defense programs will require even better laser media

DARPA - HIGH ENERGY LIQUID LASER AREA DEFENSE SYSTEM (HELLADS)
~150 kilowatt with an order-of-magnitude reduction in weight compared to existing laser systems. With a weight goal of less than five kilograms per kilowatt, HELLADS will enable high-energy lasers to be integrated onto tactical aircraft and unmanned air vehicles, and will significantly increase engagement ranges compared to ground-based systems.

Compact
Rugged
Efficient
100kW Class DPSSL
Latest Test Results

- Testing against boats in open water ignites ships engines:

- Testing against a drone in flight destroys drone:
  www.bbc.co.uk/news/world-us-canada-22076705
Scintillator Ceramics

Scintillator Applications

Detection of X-rays, γ-rays, n<sup>0</sup>, e<sup>-</sup>, p<sup>+</sup>, α, β, fission fragments,…

Medical Imaging

Homeland Security

Geological Exploration

High-Energy Physics
# Scintillator Ceramics

<table>
<thead>
<tr>
<th></th>
<th>BGO ( (\text{Bi}_4\text{Ge}<em>3\text{O}</em>{12}) )</th>
<th>LYSO:Ce ( (\text{Lu}<em>{1.8}\text{Y}</em>{0.2}\text{SiO}_5) )</th>
<th>LPS:Ce ( (\text{Lu}_2\text{Si}_2\text{O}_7) )</th>
<th>( \text{Ln}_2\text{O}_3:\text{Eu} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density</td>
<td>7.13</td>
<td>7.11</td>
<td>6.23</td>
<td>&gt;7</td>
</tr>
<tr>
<td>( \lambda_{\text{emission}} ) (nm)</td>
<td>480</td>
<td>420</td>
<td>385</td>
<td>610</td>
</tr>
<tr>
<td>Light yield (ph/MeV)</td>
<td>8,200</td>
<td>32,000</td>
<td>26,000</td>
<td>&gt;40,000</td>
</tr>
<tr>
<td>Decay time</td>
<td>300ns</td>
<td>41ns</td>
<td>38ns</td>
<td>1ms</td>
</tr>
<tr>
<td>Imaging speed</td>
<td>afterglow</td>
<td>no afterglow</td>
<td>afterglow</td>
<td>afterglow</td>
</tr>
</tbody>
</table>
Smart Gear
Future Possibilities

- Engineered ceramic gain elements for high power laser systems
- Tape casting allows for the development of Functionally Graded Materials (FGM’s)
- Possibilities: waveguides, gradient-index materials, thermal management cladding
- Achieve performance of fiber lasers in crystalline matrix

From joint White Paper: PI – Eric Honea, Aculight Corporation. Submitted 10/2/03; Team Members: VLOC, II-VI, PSU
Engineered Laser Ceramics

Example of a non-uniform doping

Transverse doping profile geometry scalable to multiple kW

Inverted population $R(x)$

Cavity mode $I(x)$
Engineered Laser Ceramics

Fabrication of dopant-engineered ceramics
(Ceramic YAG with Gradient Nd doping)

- Non-reactive sintering:
  Cold-pressing, Slip-casting, Tape-casting

- Reactive sintering:
  Cold-pressing, Slip-casting, Tape-casting

- Bonding of bulk materials:
  Ceramic – ceramic bonding
  Ceramic – single crystal bonding

Nd: 1.0 at%
Nd: 2.4 at%
Nd: 3.6 at%

Courtesy of A. Ikesue
Conclusions

- Nanopowders and nanotechnology have led to the development of a new class of solid state lasers
- In less than 15 years, powers have climbed from mW of output power, to greater than 140 kW
- Direct applications to military, biomedical, and industrial and photolithography sectors
- Volumes of material and near-net shape fabrication leading to increased throughput times
- Engineered materials should lead to new commercial laser designs
THANK YOU!

Questions?