Transparent Ceramics for Laser Gain Media - A new paradigm in advanced ceramics

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Most transparent ceramics have a cubic crystal structure

<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 components of sintered corundum with sub-µm microstructure
Light-scattering sources in transparent ceramics

- Refractive index modulation around GB
- Index changes by inclusions or pores
- Segregation of different phases
- Birefringence
- Surface scattering by roughness

After Yagi
Transparent spinel and AlON are now commercial

Spinel panel (Technology Assessment and Transfer Inc.)

AlON from Surmet Inc.
Czochralski grown Nd:YAG single crystals

- very slow growth rate (4-5 weeks)
- defect region exists
- need high temperature furnace
- requires expensive Iridium crucible
- Nd doping limited to 1.4 at% as a result of the high segregation coeff

\[ \text{Nd}_{3x} \text{Y}_{3-3x} \text{Al}_5 \text{O}_{12} \]
- cubic structure (Garnet)
- \( \text{Nd}^{3+} \) replaces \( \text{Y}^{3+} \)
- 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)
Transparent ceramics for laser gain media

• 1972 Greskovich, Woods & Chernoch – First demonstrated laser gain in a ceramic (1% Nd-89 mol%Y$_2$O$_3$ 10 mol% ThO$_2$
• 1984 de With et al. produced translucent YAG
• 1995 Ikesue reported transparent YAG in 1995, and laser generation
• 2002 Ueda, Yanagitani et al. reported laser generation in commercial YAG

Effect of porosity on YAG transparency

- Transparency is significantly affected by the residual porosity
  - Submicron pores cause scattering and reduce transparency
  - Silica doping required (0.5 wt% TEOS = 0.144 wt% SiO₂)

Porosity of $< 1.5$ ppmv is required for crystal-like transparency.

When the pore volume is less than 1.5 vol ppm, the laser performance of polycrystal specimen was nearly equal to those of single crystal. The lasing performance (threshold and slope efficiency) of ceramic specimens is clearly attributable to the pore volume.
Transparent ceramics for laser gain media

- Transparent ceramics have processing advantages relative to melt grown single crystals.
  - Relatively short processing cycle (a few days)
  - Do not need iridium crucible for melting
  - Homogeneous composition

Konoshima Chemical Co. Ltd, Nd:YAG (100 x 100 x 11 mm)
Transparent YAG ceramics for high power lasers

The optical and laser properties are equivalent to or better than YAG single crystal
Commercial Nd:YAG ceramic for high power lasers

After Ueda

10 x 10 x 2 cm slabs of Nd:YAG; ST&R 10-17 (April 2006)
Injection molded Optical ceramics (Toshiba Ceramics Inc.)

Ceramic YAG laser for Backlighting source of LCD-TV. Consumer market oriented. <$100

2nd LCS Symposium In Tokyo, UEC Nov. 10-12, 2006

After Ueda
Papers about transparent ceramics

![Graph showing citations over years for "Transparent Ceramic" and "Transparent YAG" keywords.]

Citations

Year

## Polycrystalline ceramic YAG process

<table>
<thead>
<tr>
<th></th>
<th>Co-precipitation</th>
<th>Reactive sintering</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Company</strong></td>
<td>Konoshima (Yanagitani, Yagi, Ueda)</td>
<td>JFCC &amp; Polytechno Co. (Ikesue)</td>
</tr>
<tr>
<td><strong>Powder</strong></td>
<td>Coprecipitate metal chloride</td>
<td></td>
</tr>
<tr>
<td></td>
<td>- complex process</td>
<td>Oxide powder from alkoxide</td>
</tr>
<tr>
<td></td>
<td>- difficult to scale up</td>
<td>- easy process</td>
</tr>
<tr>
<td><strong>Calcination</strong></td>
<td>1200-1300°C</td>
<td></td>
</tr>
<tr>
<td><strong>Forming</strong></td>
<td>Slip casting</td>
<td></td>
</tr>
<tr>
<td><strong>Sintering</strong></td>
<td>Vacuum in metal furnace</td>
<td></td>
</tr>
<tr>
<td><strong>Grain size</strong></td>
<td>&lt; 5 μm</td>
<td>Not necessary</td>
</tr>
<tr>
<td><strong>Laser generation</strong></td>
<td>1.46 KW</td>
<td>Dry pressing (spray dried powder)</td>
</tr>
<tr>
<td><strong>Patent</strong></td>
<td>JP 10-101333, JP 10-101411</td>
<td>Vacuum in metal furnace</td>
</tr>
<tr>
<td></td>
<td></td>
<td>20-30 μm</td>
</tr>
<tr>
<td></td>
<td></td>
<td>700 Watt</td>
</tr>
<tr>
<td></td>
<td></td>
<td>JP 03-218963 (by Krosaki)</td>
</tr>
</tbody>
</table>

**Konoshima, 8 at% Nd:YAG**

**Ikesue 1.1 at% Nd:YAG**

Stoichiometry is a major processing challenge for YAG laser gain media

Densification and grain growth of pure YAG ($t = 2\,\text{h}$)

Sintering activation energy = 237 kJ/mol
Grain growth activation energy = 946 kJ/mol

Fig. 3. SEM micrographs of pure YAG sintered for 2 h at (a) 1484 °C, (b) 1564 °C, (c) 1696 °C at

Pore size and pore number per volume for pure YAG

Densification of silica doped (0.144 wt%) and pure YAG

SiO$_2$ doped YAG ($T = 1484-1850$°C)

Fig. 7. SEM micrographs of SiO$_2$ doped YAG sintered for 2 h at (a) 1484 °C, (b) 1606 °C, (c) 1745 °C and (d) 1850 °C.
Densification of Nd$_2$O$_3$ : YAG

All samples contain 0.144 wt% silica except Pure.  
S. Kochawattana, A. Stevenson, et al,  
Microstructures of \( \text{Nd}_2\text{O}_3 : \text{YAG} \) \((t = 2 \text{ h})\)

All samples contain 0.144 wt% silica

0\% Nd:YAG

![Microstructure Images](image1)

1\% Nd:YAG

![Microstructure Images](image2)

Microstructures of $\text{Nd}_2\text{O}_3:Y\text{AG}(t = 2 \text{ h})$

All samples contain 0.5 wt% of TEOS.

5% Nd:YAG

- 1606°C 2h
  - 99.61 %
- 1696°C 2h
  - 99.98 %
- 1796°C 2h
  - 100.00 %

9% Nd:YAG

- 1606°C 2h
  - 99.47 %
- 1696°C 2h
  - 99.95 %
- 1796°C 2h
  - 100.00 %

Grain growth of Nd$_2$O$_3$:YAG YAG (t = 2 h)

All samples contain 0.144 wt% silica except Pure.

Confocal microscopy of 1% Nd:YAG ceramics

Fluorescence Mapping (Confocal & NSOM)

Confocal Raman Spectroscopy

M. O. Ramirez et al, Optics Express 16 (9), pp. 5965-5973 (2008)
Eye safer composite ceramic laser gain media

• **Approach**
  - Material: Er:YAG (lases at 1.64 μm – eye safer)
  - Composite architecture for thermal management
    - Rod geometry with pure YAG at pump ports, Er:YAG for lasing
    - Composite structures formed in the green state

• **Analysis**
  - Confocal scanning optical microscopy (CSOM)
  - Bulk optical characterization (transmittance, absorption and emission cross sections)
Tape casting* of YAG composites

- RE dopant
- $\text{Y}_2\text{O}_3$
- $\text{Al}_2\text{O}_3$
- Solvent
- Dispersant
- Processing polymers (binder/plasticizer)

**Process Steps:**
1. Mill
2. Add
3. Mill
4. Cast Tape
5. Laminate and burn out organics
6. Sinter
7. HIP

*Patent application filed (Method for Manufacture of Transparent Ceramics)
Composite manufacture*

- Stacked composites - cast individual compositions and stack them to make layered parts

- Co-cast composites - simultaneously cast three slurries and stack tape layers to make slabs

*Patent application filed (Method for Manufacture of Transparent Ceramics)
Pure YAG part (45 x 45 x 3 mm)

Sinter conditions: 1800°C/16 hr/vac
Visual transparency of a composite slab

Photograph through the length of a 3.5 x 12 x 60 mm co-cast ceramic composite Er:YAG slab

Printed image

End face of slab (60 mm above printed image)
Er:YAG composite microstructure

SEM images of each composition in a co-cast Er:YAG composite (average grains sizes are 2-2.5 μm)

- Pure YAG
- 0.25% Er:YAG
- 0.5% Er:YAG
Er gradient across the co-cast composite

Length of 0.25% plateau is actually 16 mm (16,000 μm)
Visual Confirmation of the dopant concentration distribution in an Er:YAG composite rod

Direction of the 1532-nm laser excitation (arrow)

Clear manifestation of the three-step doping in a co-cast Er:YAG ceramic composite rod via Er$^{3+}$ upconversion processes

Green glow - upconversion based
In-Line transmittance of a co-cast Er:YAG composite slab

At 1064 nm, transmittance is:
- Pure YAG – 84%
- 0.25% Er:YAG – 83.6%
- 0.5% Er:YAG – 82.7%

Theoretical transmittance (84%)
## Transparent YAG Ceramics Developed at Penn State

<table>
<thead>
<tr>
<th>Sample Description</th>
<th>Diameter (mm)</th>
<th>Thickness (mm)</th>
<th>Composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.50% Nd:YAG</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.25% Er:YAG</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pure YAG</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Segmented Er:YAG composite slab (tape cast), 12 x 60 x 3.5 mm</td>
<td>12</td>
<td>3.5</td>
<td></td>
</tr>
<tr>
<td>1% Er:YAG (dry pressed), 22 mm φ x 4 mm thick</td>
<td>22</td>
<td>4</td>
<td></td>
</tr>
<tr>
<td>1% Nd:YAG (slip cast), 78 mm φ x 5 mm thick</td>
<td>78</td>
<td>5</td>
<td></td>
</tr>
<tr>
<td>Stacked Er:YAG composite (tape cast), 25 x 25 x 3 mm</td>
<td>25</td>
<td>3</td>
<td>(0/0.25/0.50% Er:YAG – bottom to top)</td>
</tr>
<tr>
<td>Pure YAG</td>
<td>45</td>
<td>3</td>
<td></td>
</tr>
<tr>
<td>0.25% Er:YAG</td>
<td>22</td>
<td>3</td>
<td></td>
</tr>
<tr>
<td>0.50% Er:YAG</td>
<td>22</td>
<td>3</td>
<td></td>
</tr>
</tbody>
</table>
Summary

• Transparent ceramics have a bright future

• Bridges between processing and user communities will ensure more rapid advances

• Processing innovation will enable access to numerous unforeseen optical products

• Confocal microscopy allows unique perspectives on grain boundary chemistry

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“Where did I put that screw?”
“It’s in here somewhere”
“I think I’ve got it”
“Gary, Can you help me out of here?”
“Gary, That sweatshirt looks good on you”
Trying to look like Ludwig
Mapping the Rund Um course
“The water is warm. Come on in!”
“Hang on!”
“Gary, Isn’t sailboat racing fun?”
See, I told you this would be fun.
Thumbs up!
Still smiling
Sailing without wind
He does rest!
His pride and joy
Thank you Ludwig and Gisela