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

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Most transparent ceramics have a cubic crystal structure

Material	Composition	Crystal Structure
Yttrium Aluminum Garnet	$3Y_2O_3 \cdot 5Al_2O_3$	cubic
Yttria	Y_2O_3	cubic
Scandium oxide	Sc_2O_3	cubic
Lutetium oxide	Lu_2O_3	cubic
AlON	AlON	cubic
Spinel	$MgO \cdot Al_2O_3$	cubic
Zinc sulfide	ZnS	cubic
Alumina (Lucalox)	Al_2O_3	rhombohedral

Spinel dome (Surmet)

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Transparent components of sintered corundum with sub-µm microstructure

Fraunhofer IKTS
Institut
Keramische Technologien
und Sinterwerkstoffe

Light-scattering sources in transparent ceramics

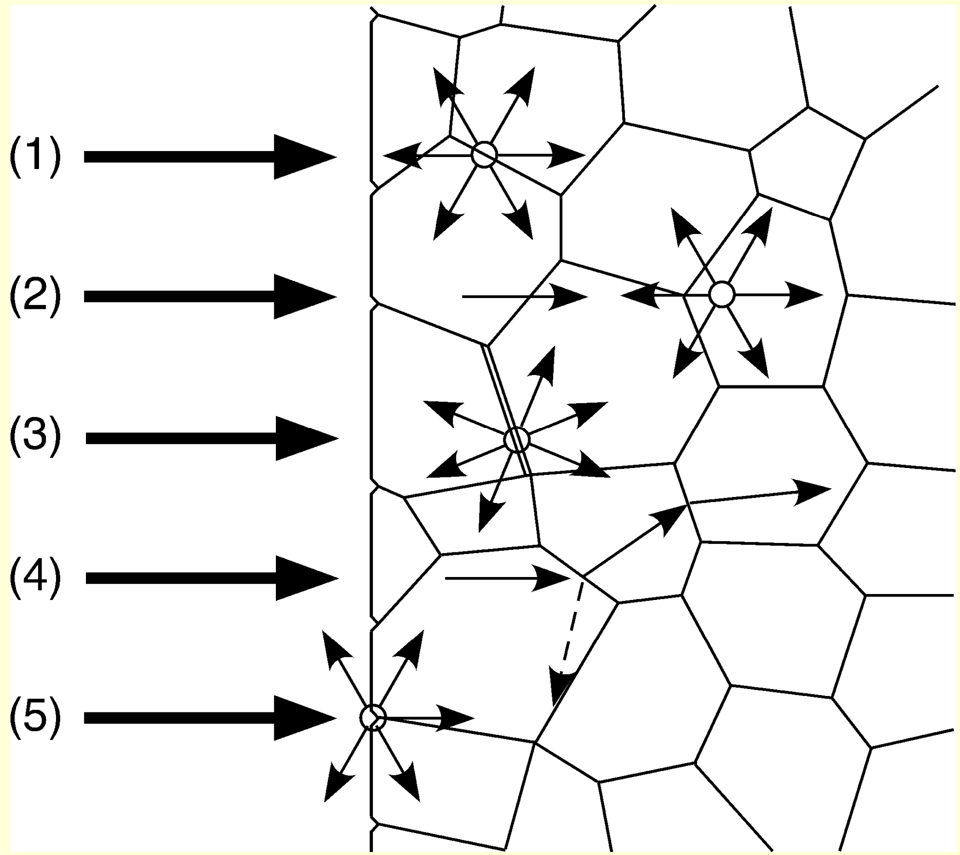
Refractive index modulation around GB

Index changes by inclusions or pores

Segregation of different phases

Birefringence

Surface scattering by roughness



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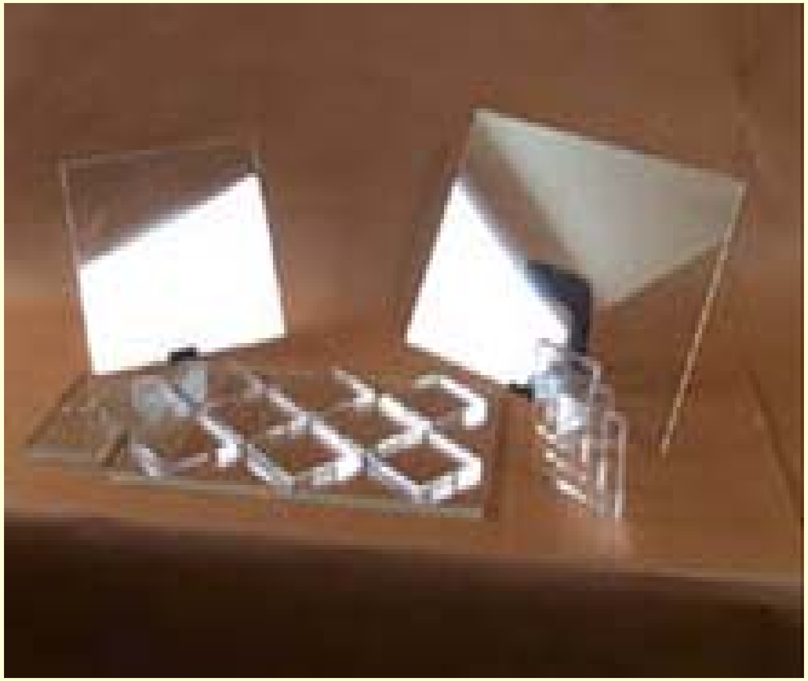
After Yagi

Transparent spinel and AlON are now commercial

Spinel panel (Technology Assessment and Transfer Inc.)



AlON from Surmet Inc.

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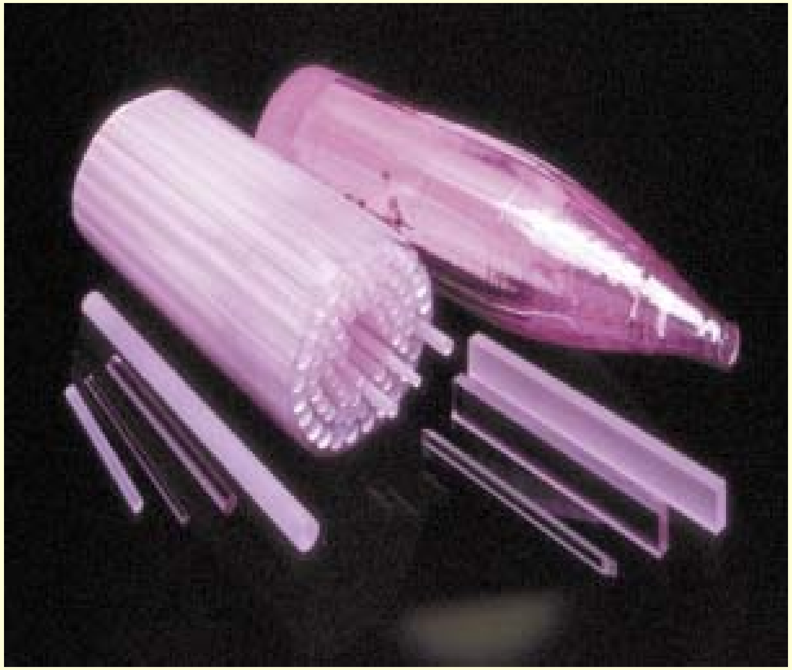
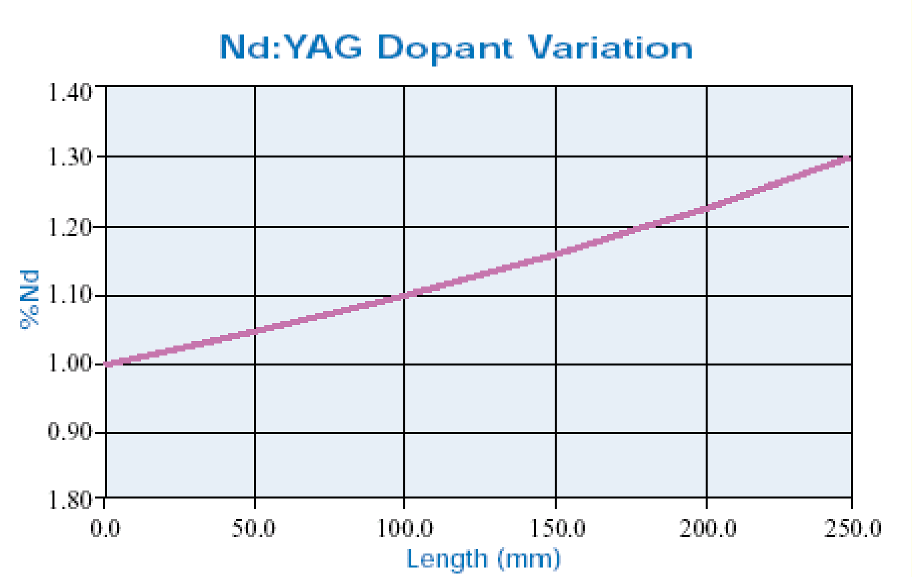
Czochralski grown Nd:YAG single crystals



- 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

$Nd_{3x}Y_{3-3x}Al_5O_{12}$

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



only 25% of melt can be used

(Ref. Yttrium Aluminum Garnet Laser Materials, VLOC brochure)

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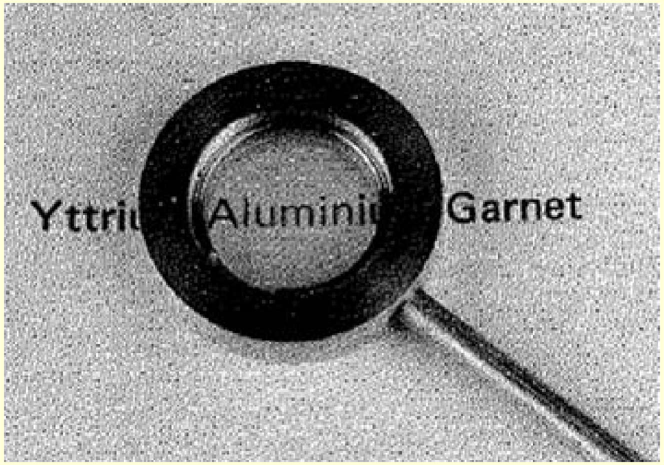
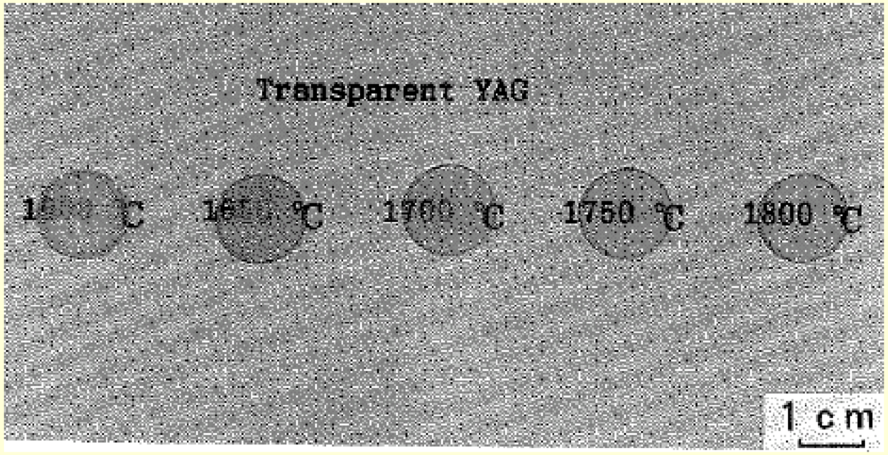
Transparent ceramics for laser gain media

- 1972 Greskovich, Woods & Chernoch – First demonstrated laser gain in a ceramic (1% Nd-89 mol%$Y_2O_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



de With et al., *Mat. Res. Bull.* **19**, 1669-74 (1984)



Ikesue et al. *J. Am. Ceram. Soc.*, **78** 225-28 (1995)

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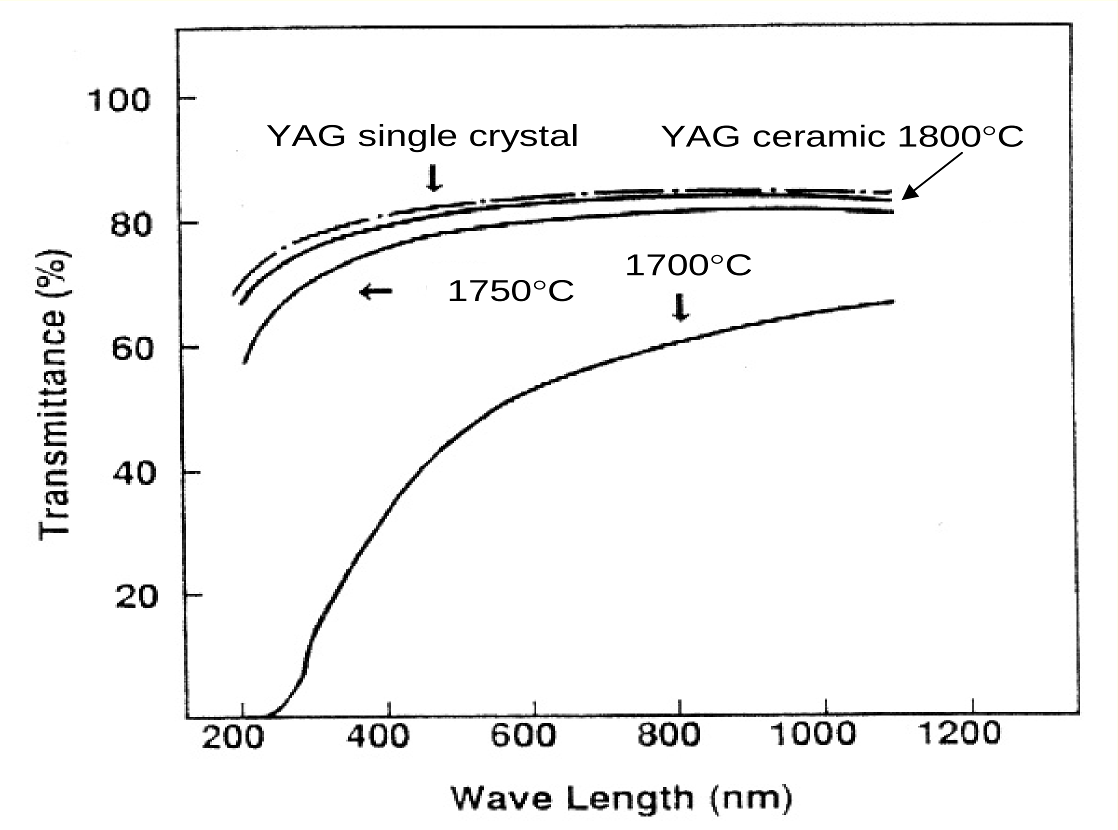
Effect of porosity on YAG transparency

- **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% SiO_2)



(Ikesue et al. J. Am.Ceram. Soc. 1995)

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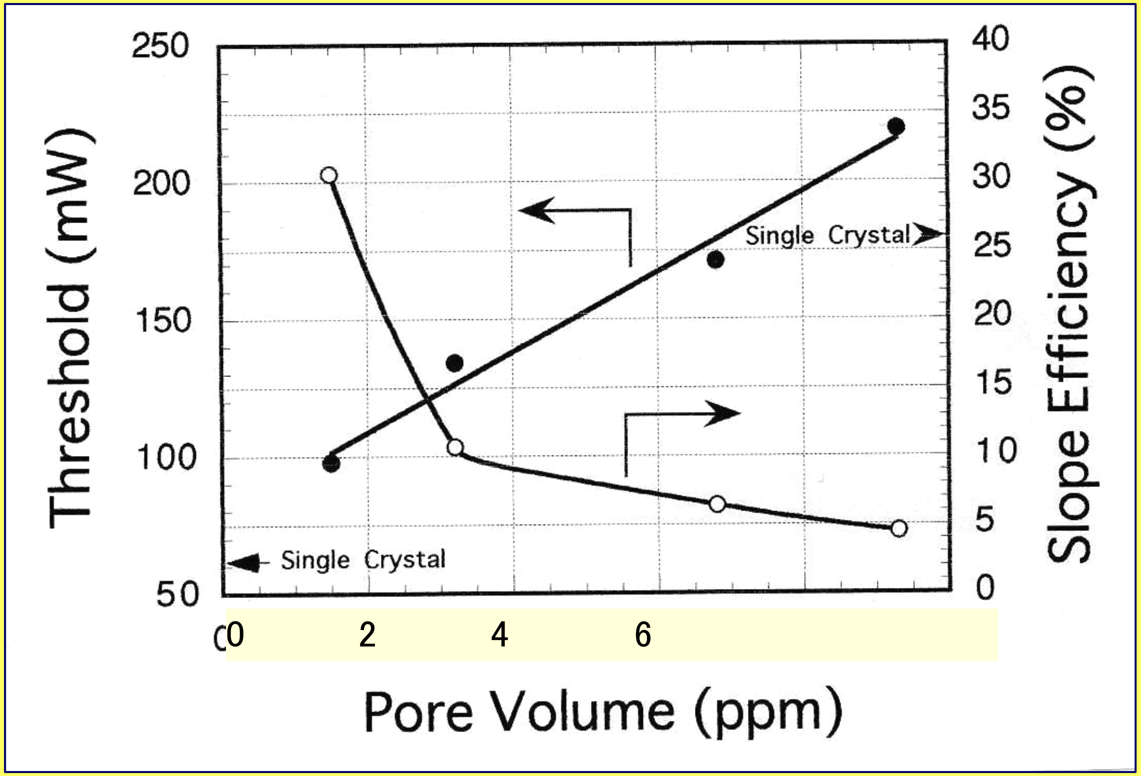
Porosity of < 1.5 ppmv is required for crystal-like transparency

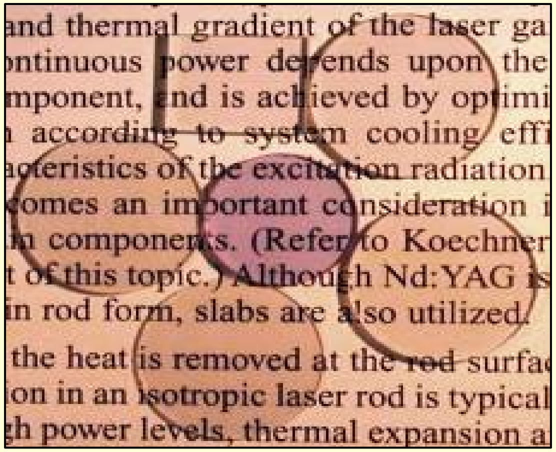


When the pore volume is less than 1.5 vol ppm, the laser performance of polycrystal specimen was nearly equal to those of single crystal. The lasing performance (threshold and slope efficiency) of ceramic specimens is clearly attributable to the pore volume.

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)



Konoshima Chemical Co. Ltd: cw from top: Yb:YAG; Y_2O_3; Sc_2O_3; Yb:Y_2O_3; Yb:Sc_2O_3; Nd:Y_2O_3

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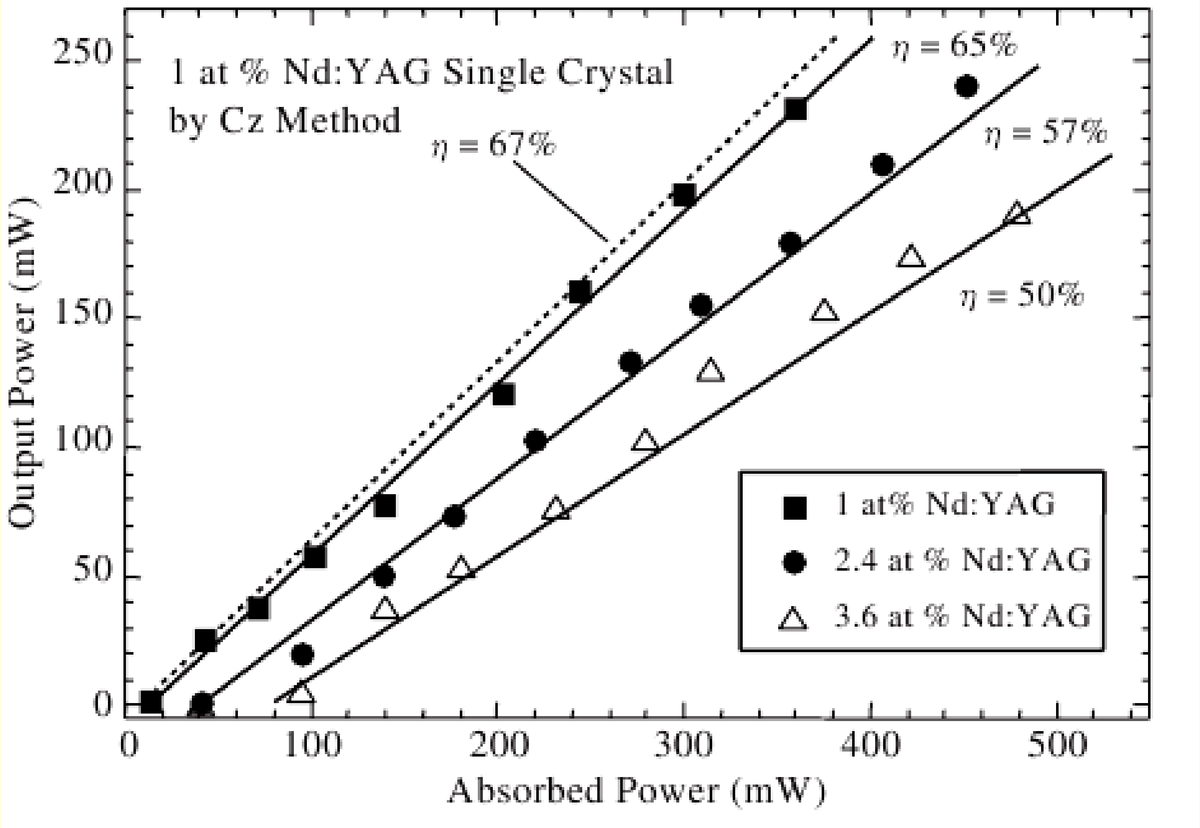
Transparent YAG ceramics for high power lasers

The optical and laser properties are equivalent to or better than YAG single crystal



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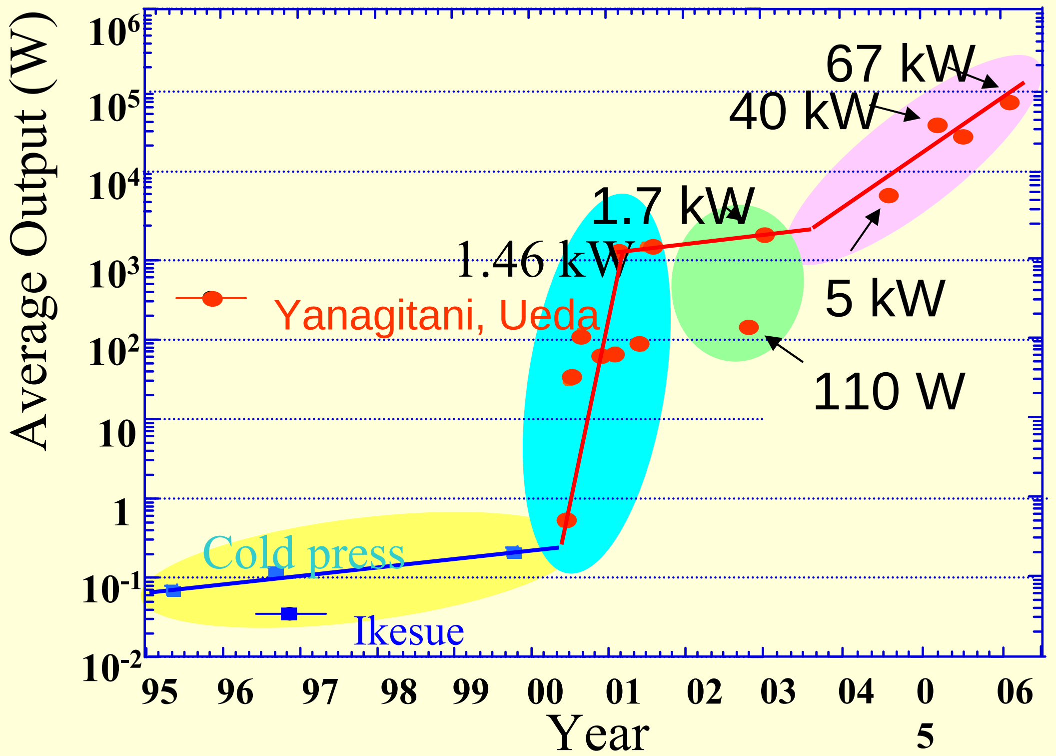
A. Ikesue and Y. L. Aung, J. Am. Ceram. Soc. 89 [6], 1936-1944 (2006).

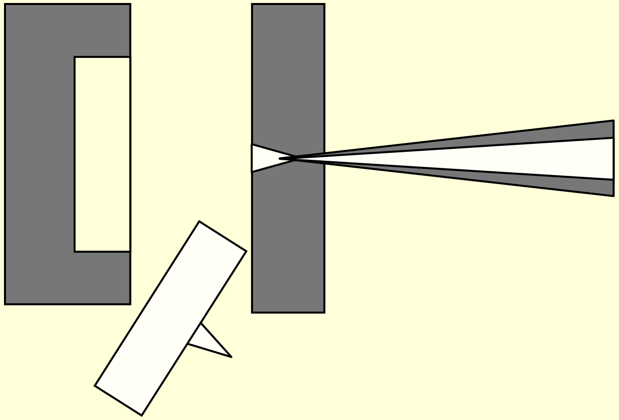
Commercial Nd:YAG ceramic for high power lasers



10 x 10 x 2 cm slabs of Nd:YAG; ST&R 10-17 (April 2006)

After Ueda

Injection molded optical ceramics (Toshiba Ceramics Inc.)

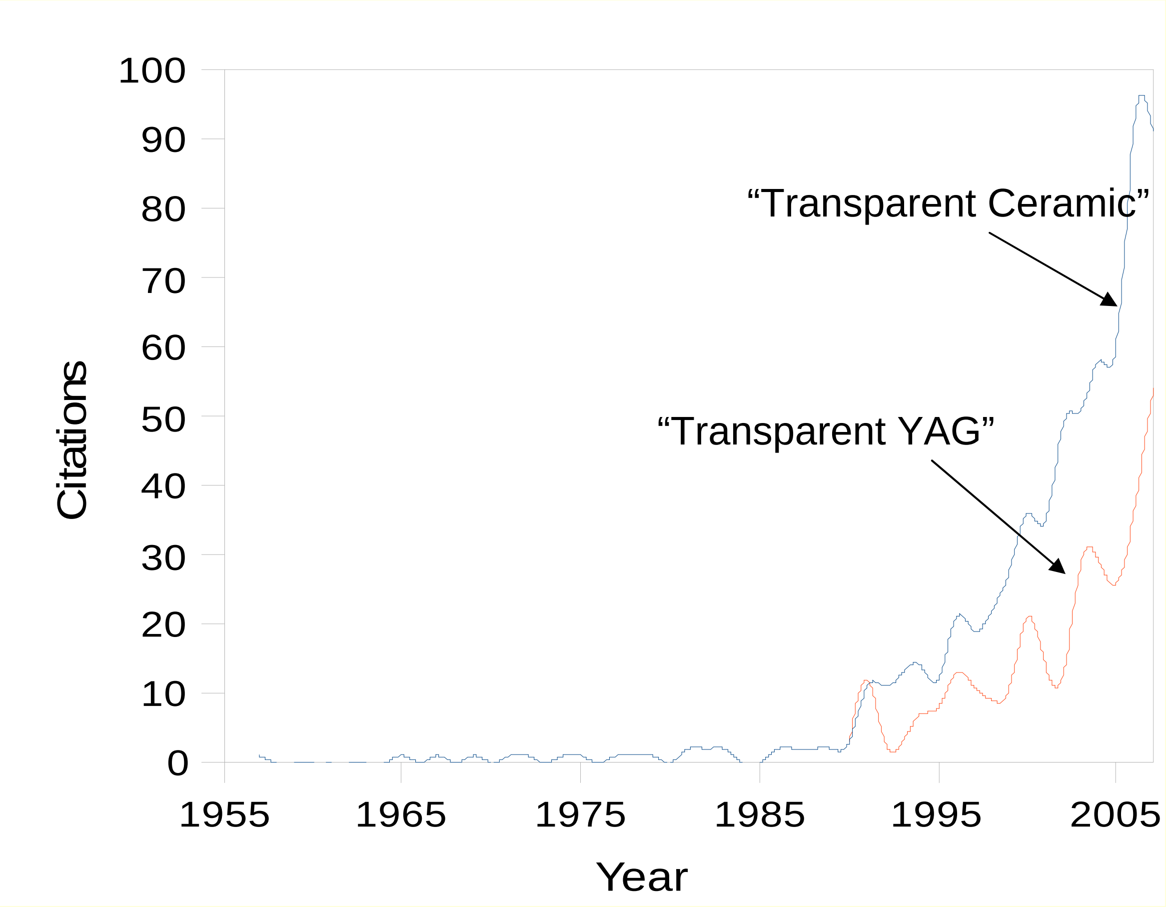


2nd LCS Symposium
In Tokyo, UEC
Nov. 10-12, 2006

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

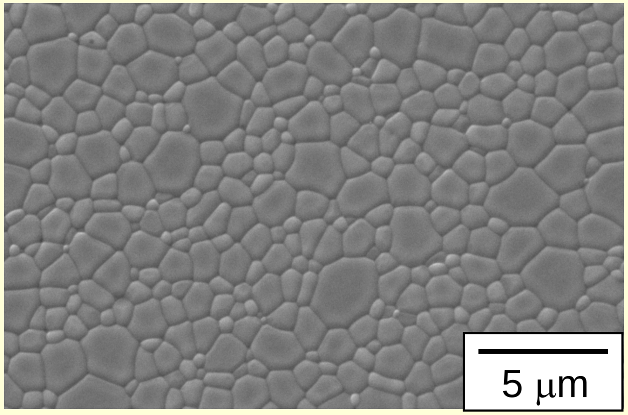
After Ueda

Papers about transparent ceramics

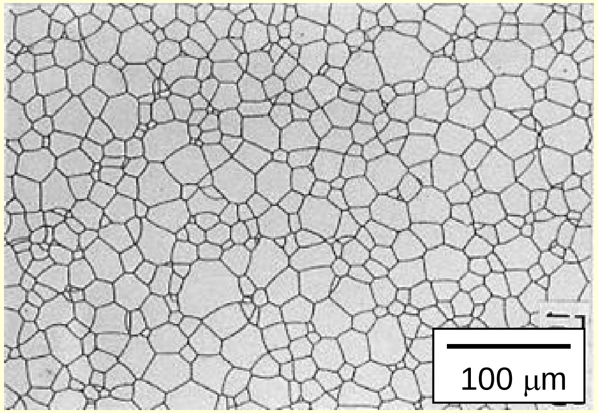


Polycrystalline ceramic YAG process

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



Konoshima, 8 at% Nd:YAG



Ikesue 1.1 at% Nd:YAG

J. Am. Ceram. Soc, **78** 1033-40 (1995)

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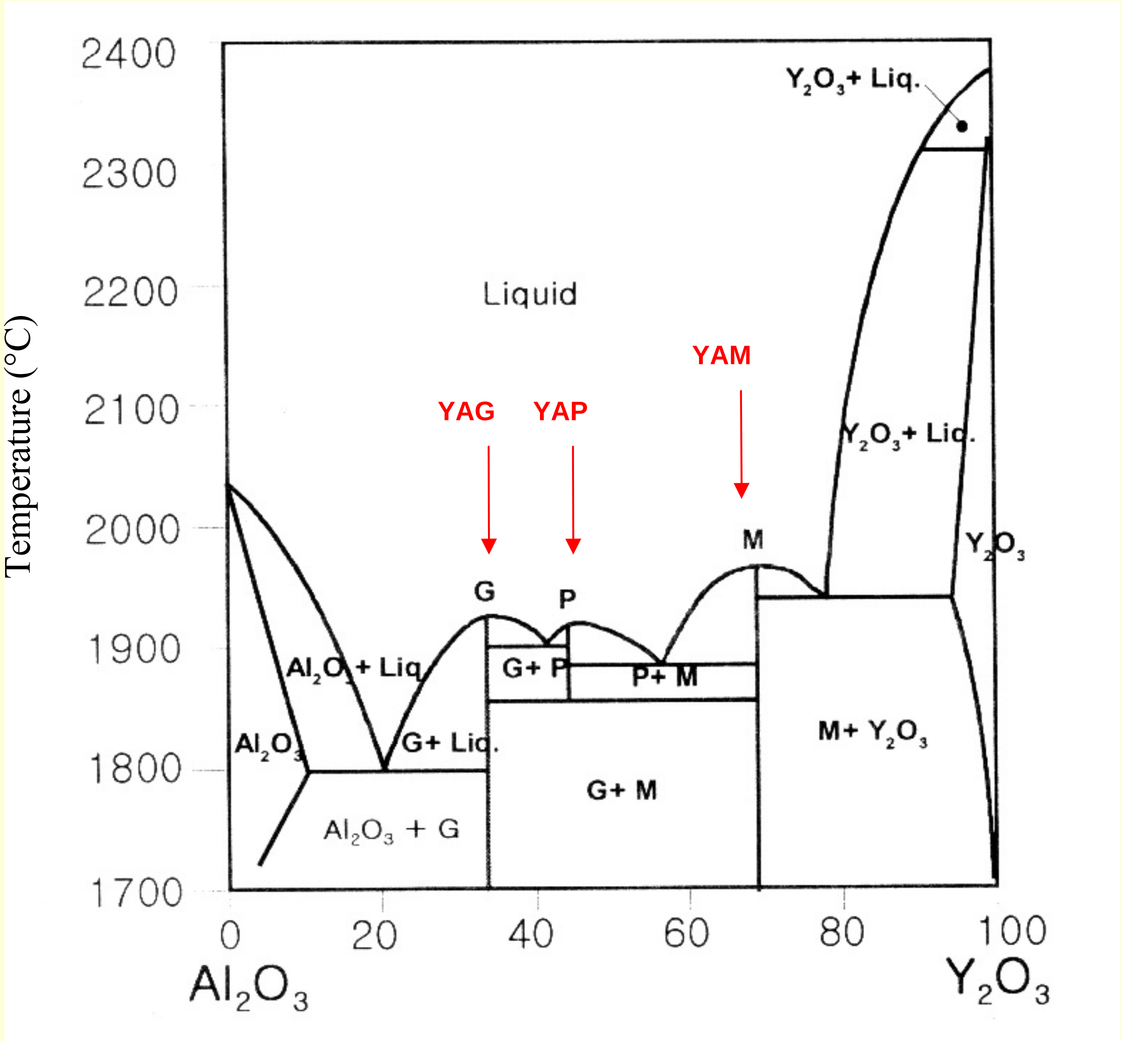
Stoichiometry is a major processing challenge for YAG laser gain media



M. Mizuno and T. Noguchi, *Gept. Govt. Ind. Res. Inst. Nagoya*, 16, 171 (1967).

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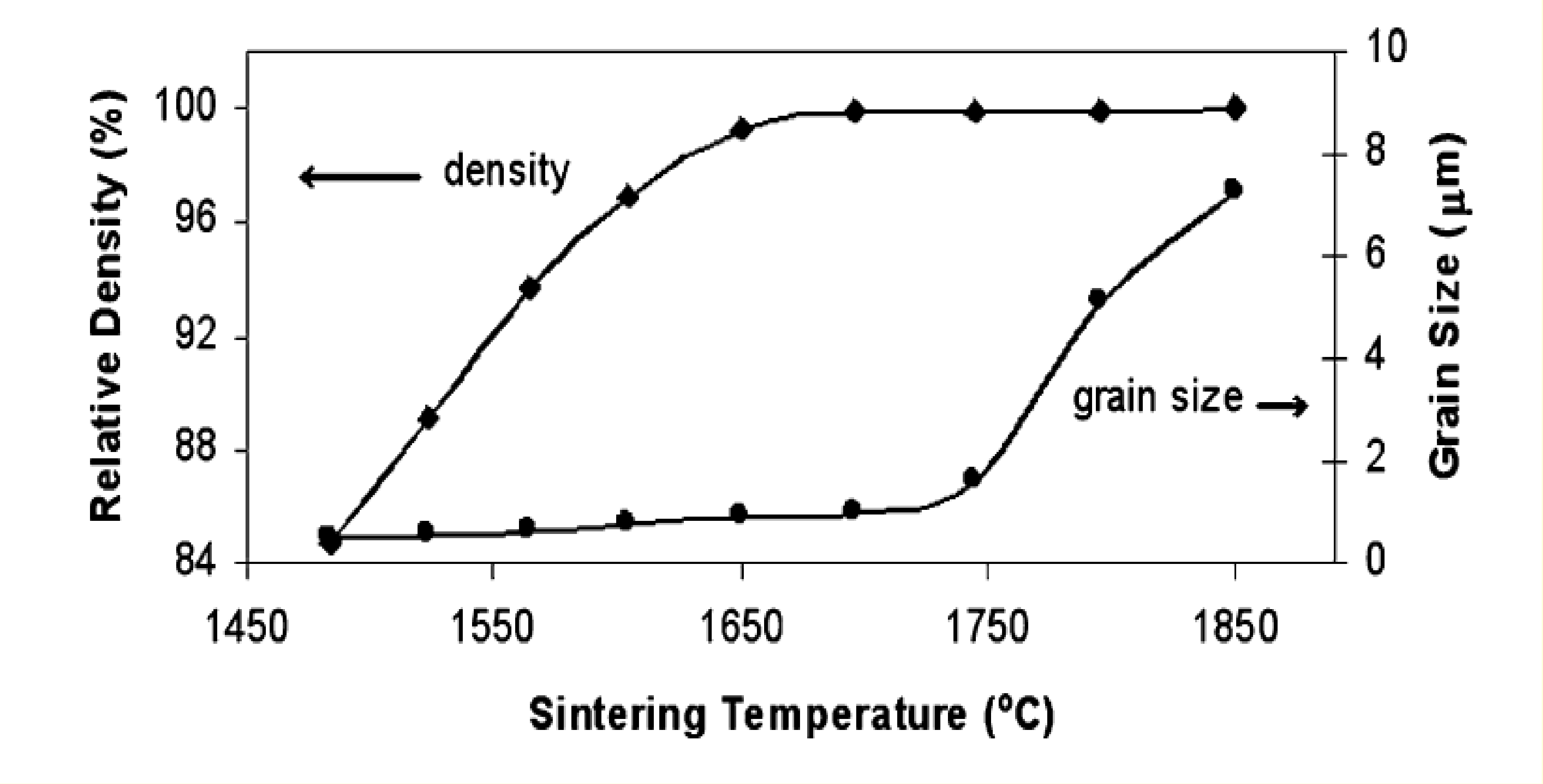
Densification and grain growth of pure YAG (t = 2 h)



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

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S. Kochawattana, A. Stevenson, et al,
J. Eur Cer Soc 28 1527-1534 (2008).

Microstructures of pure YAG (T = 1484-1696C)

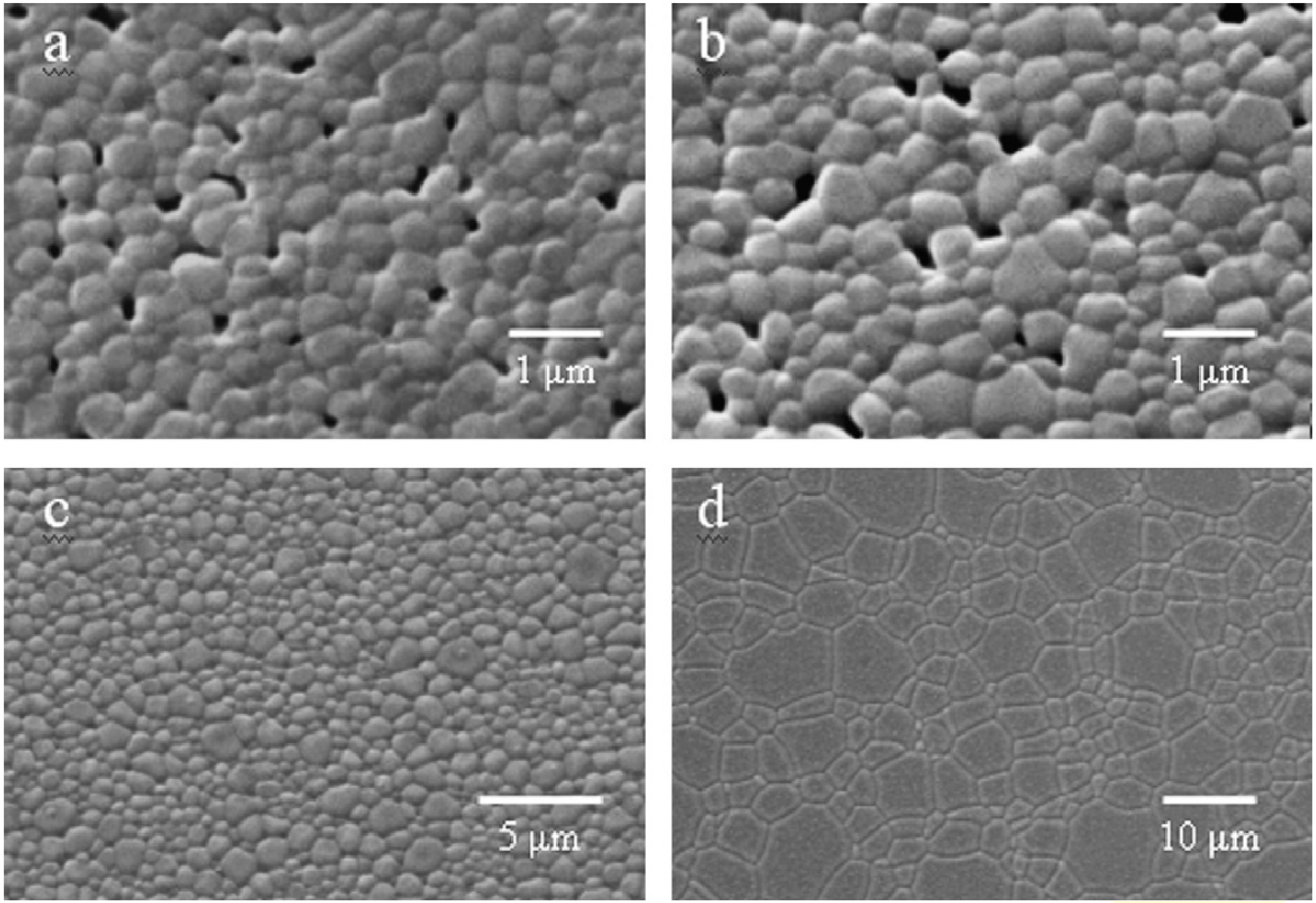

Fig. 3. SEM micrographs of pure YAG sintered for 2 h at (a) 1484 °C, (b) 1564 °C, (c) 1696 °C ar

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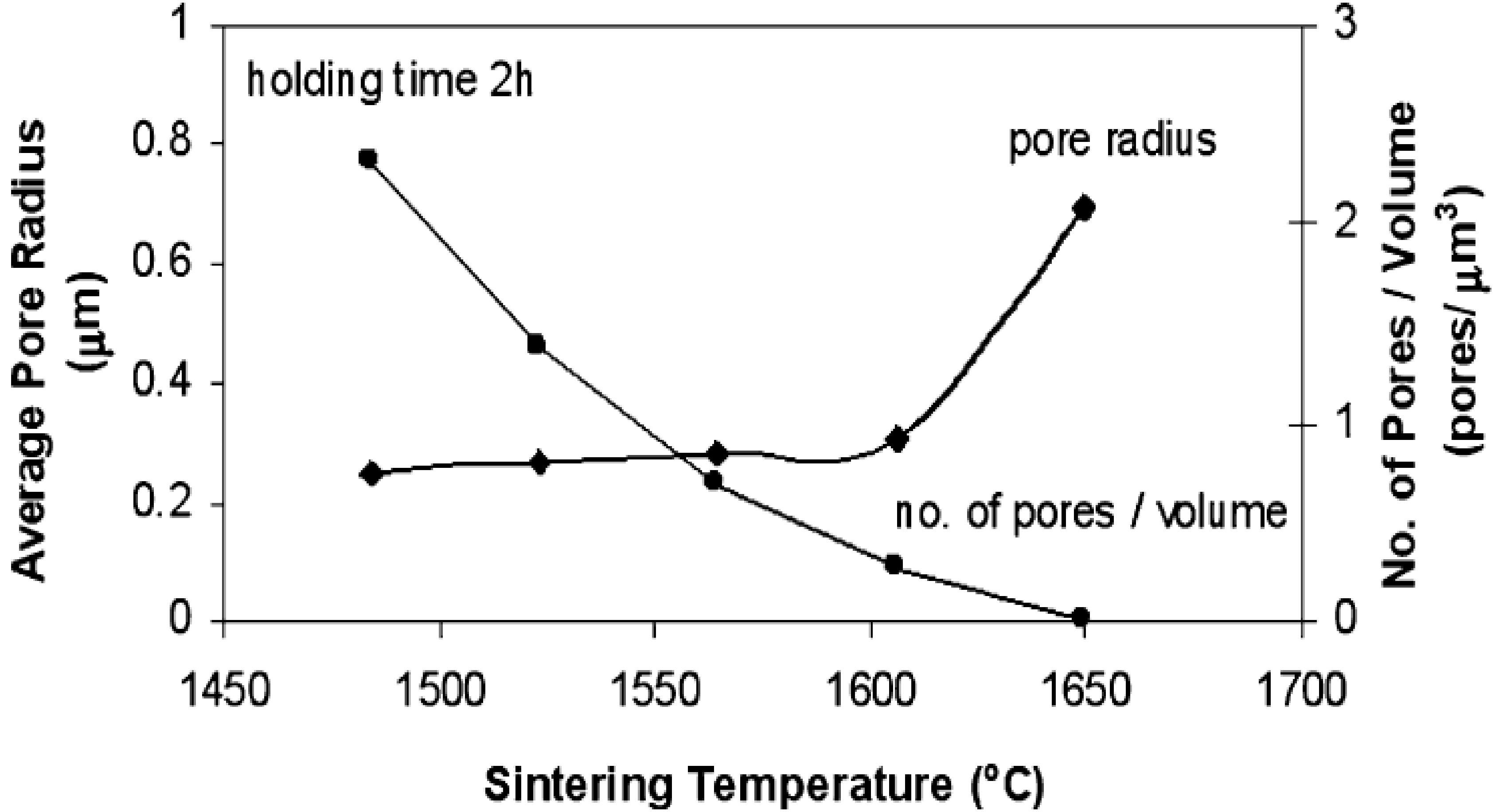
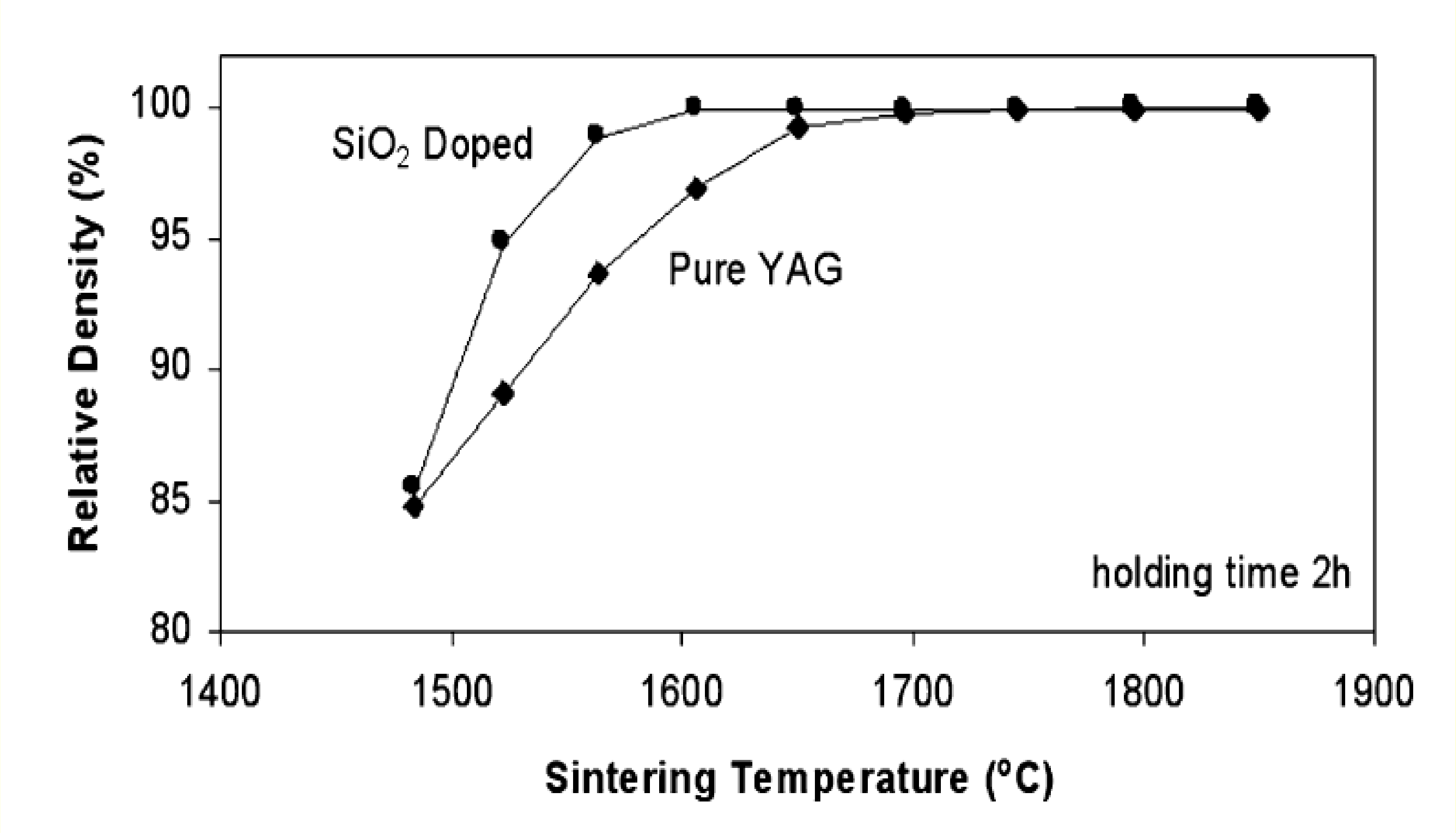
S. Kochawattana, A. Stevenson, et al,
J. Eur Cer Soc 28 1527-1534 (2008).

Pore size and pore number per volume for pure YAG



S. Kochawattana, A. Stevenson, et al,
J. Eur Cer Soc 28 1527-1534 (2008).

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



S. Kochawattana, A. Stevenson, et al,
J. Eur Cer Soc 28 1527-1534 (2008).

SiO_2 doped YAG (T = 1484-1850C)

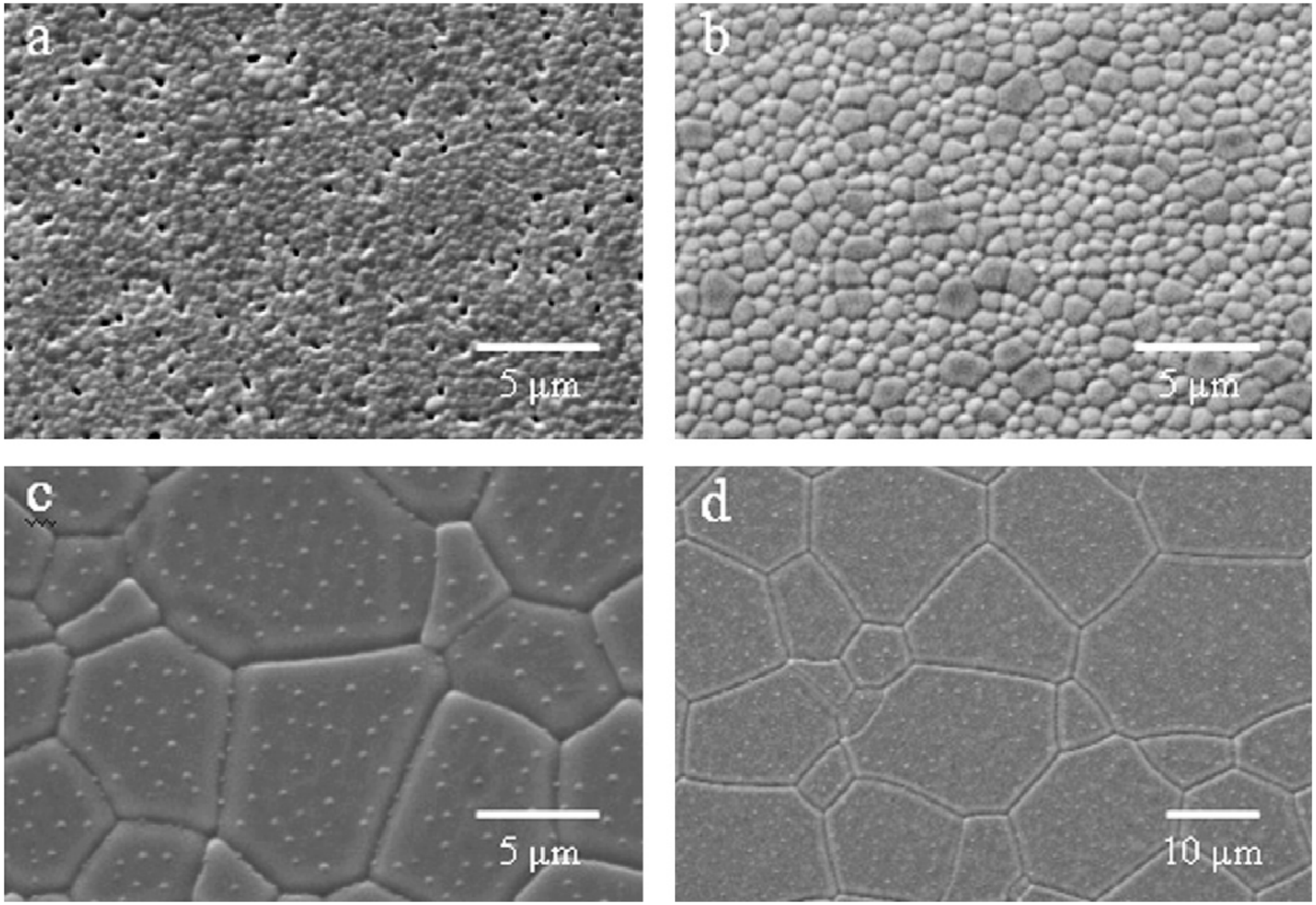


Fig. 7. SEM micrographs of SiO_2 doped YAG sintered for 2 h at (a) 1484 °C, (b) 1606 °C, (c) 1745 °C and (d) 1850 °C.

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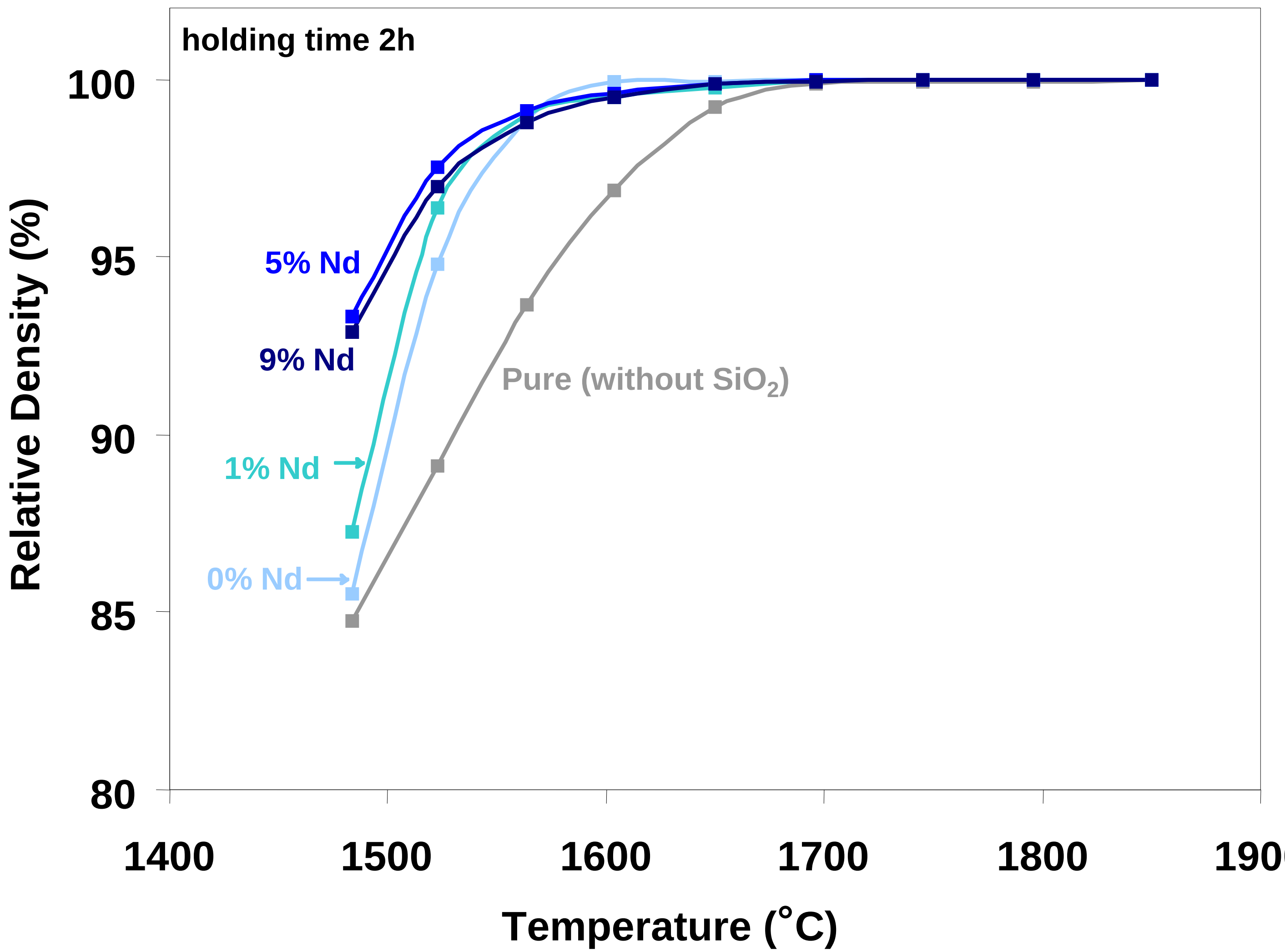
S. Kochawattana, A. Stevenson, et al,
***J. Eur Cer Soc* 28 1527-1534 (2008).**

Densification of Nd_2O_3:YAG



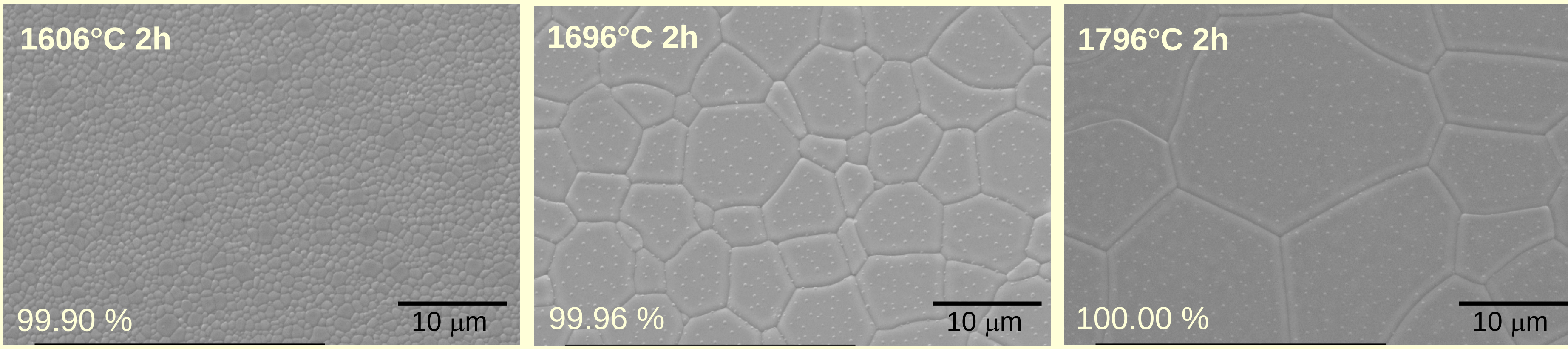
All samples contain 0.144 wt% silica except Pure.

S. Kochawattana, A. Stevenson, et al, *J. Eur Cer Soc* 28 1527-1534 (2008).

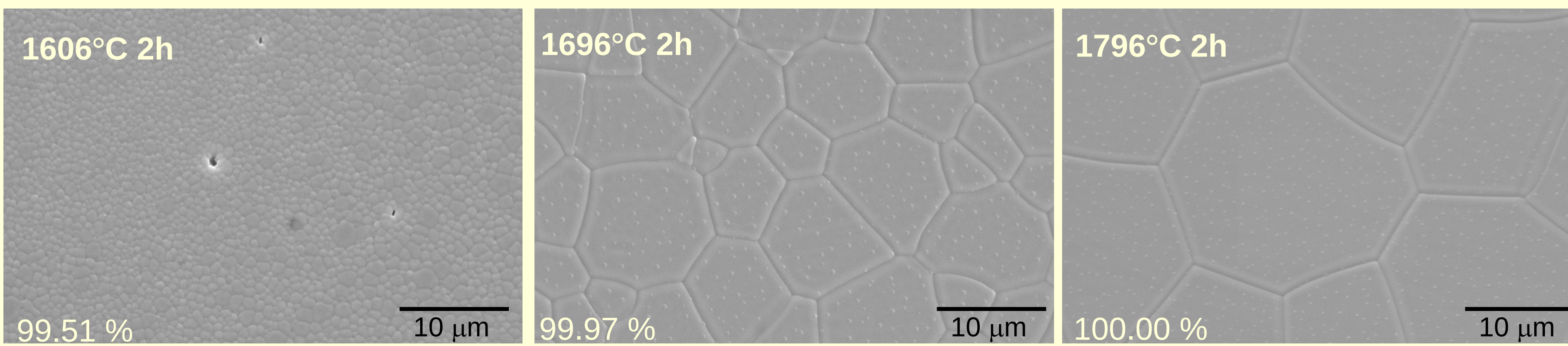
Microstructures of Nd_2O_3:YAG (t = 2 h)

All samples contain 0.144 wt% silica

0% Nd:YAG



1% Nd:YAG



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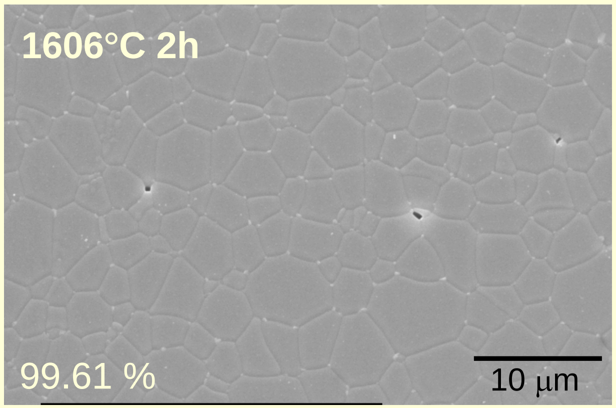
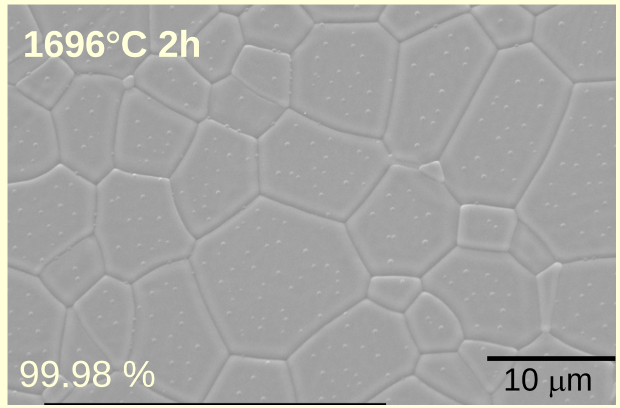
S. Kochawattana, A. Stevenson, et al,
***J. Eur Cer Soc* 28 1527-1534 (2008).**

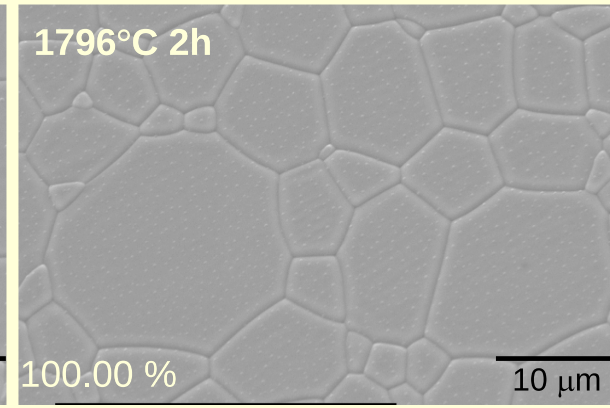
Microstructures of Nd_2O_3:YAG (t = 2 h)

All samples contain 0.5 wt% of TEOS.

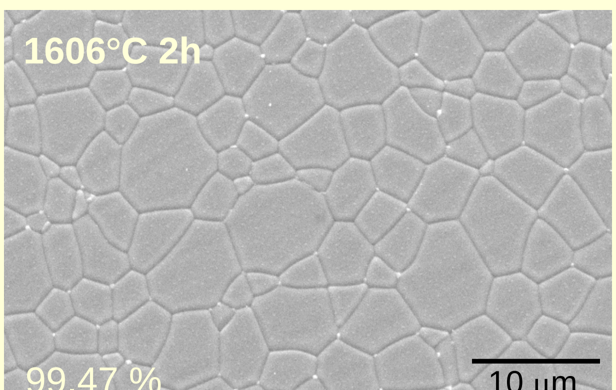
5% Nd:YAG

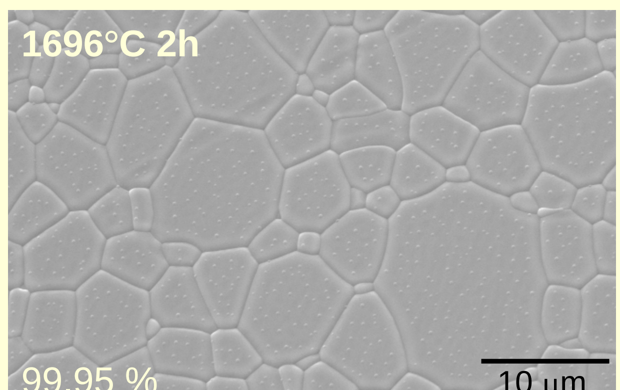


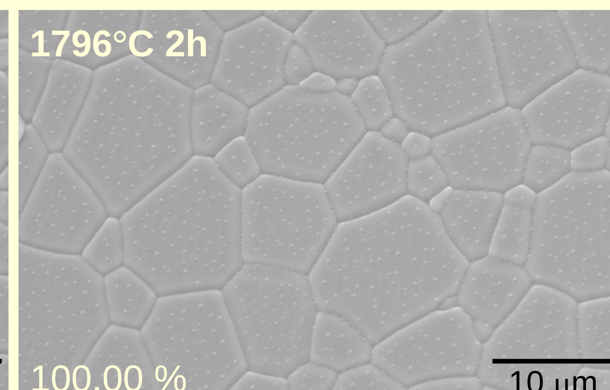




9% Nd:YAG







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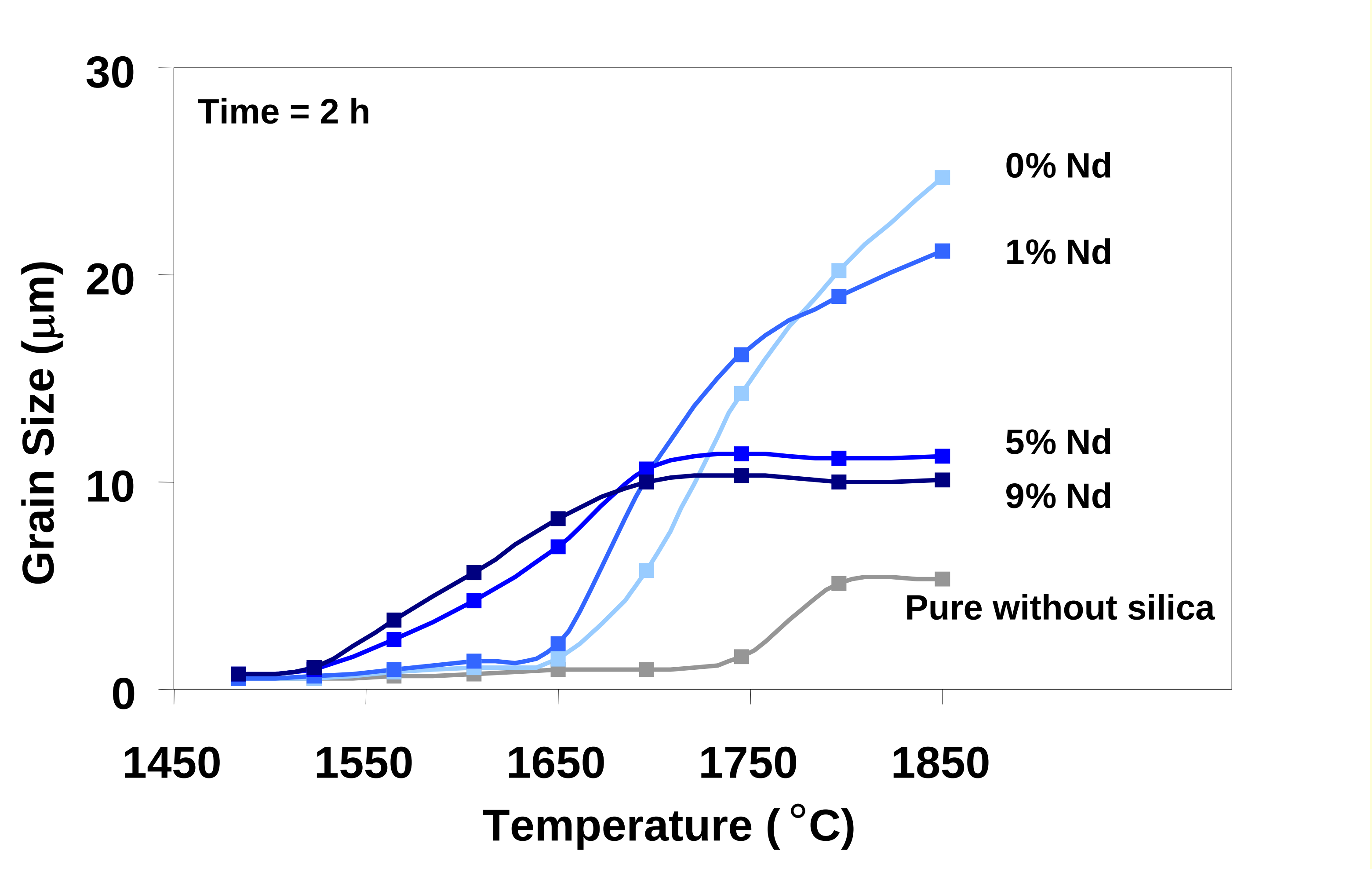
S. Kochawattana, A. Stevenson, et al, *J. Eur Cer Soc* 28 1527-1534 (2008).

Grain growth of Nd_2O_3:YAG YAG (t = 2 h)



All samples contain 0.144 wt% silica except Pure.

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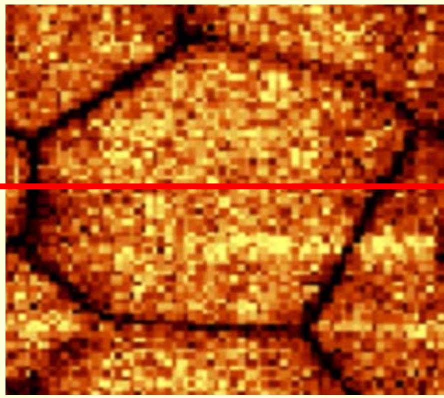
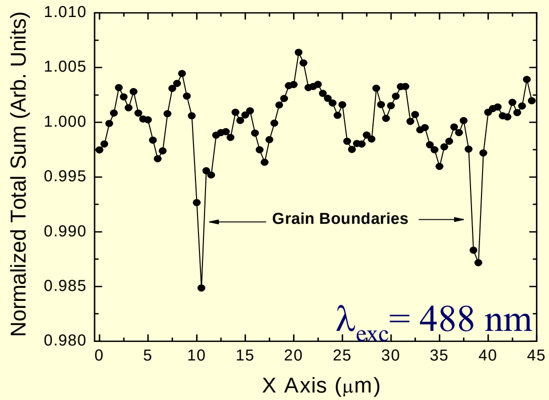
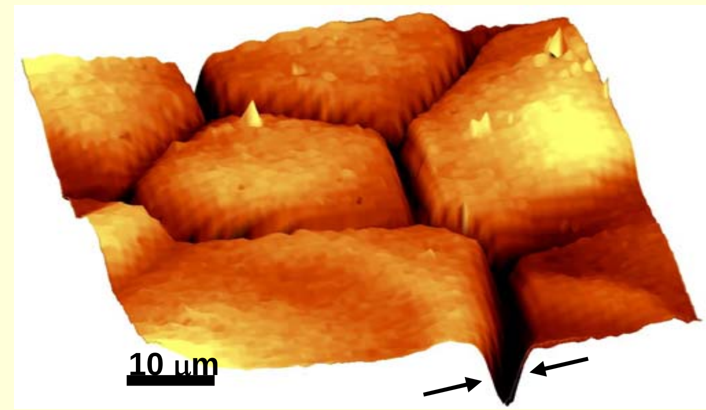
S. Kochawattana, A. Stevenson, et al, *J. Eur Cer Soc* 28 1527-1534 (2008).

Confocal microscopy of 1% Nd:YAG ceramics

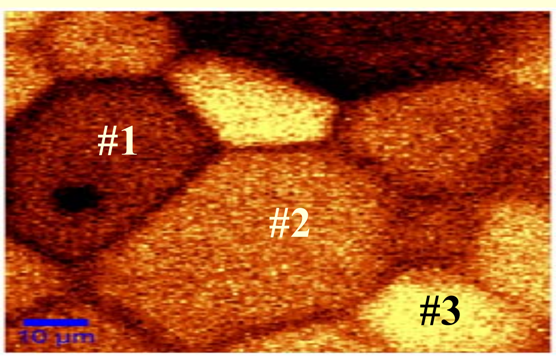
Fluorescence Mapping (Confocal & NSOM)

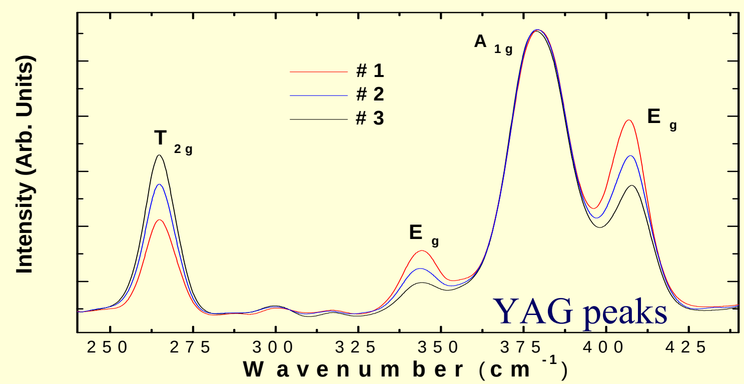






Confocal Raman Spectroscopy

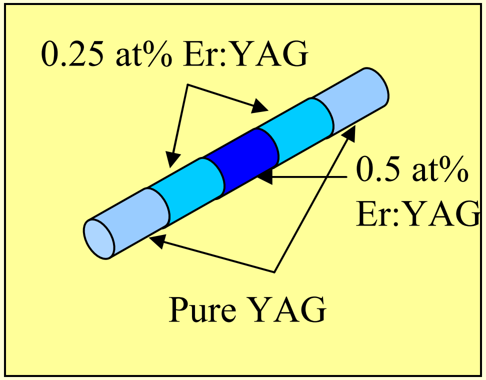




M. O. Ramirez et al, *Optics Express* 16 (9), pp. 5965-5973 (2008)

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)

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Tape casting* of YAG composites

RE dopant, **Y_2O_3**, **Al_2O_3** → **Mill** ← **Solvent**, **Dispersant**

Mill — Add — **Processing polymers (binder/plasticizer)**

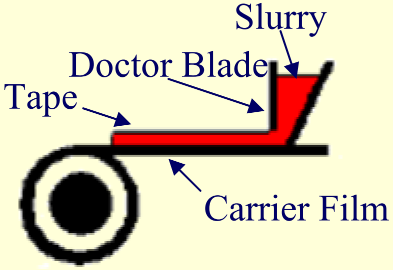
Mill

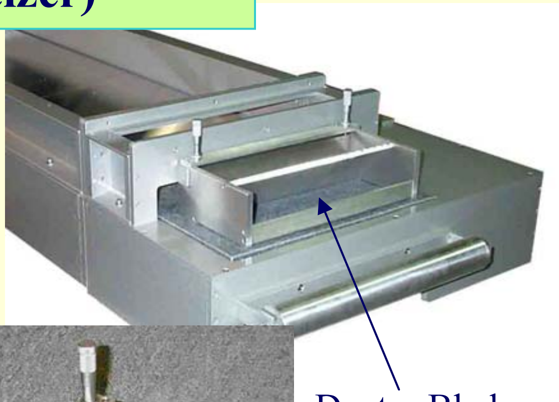
Cast Tape

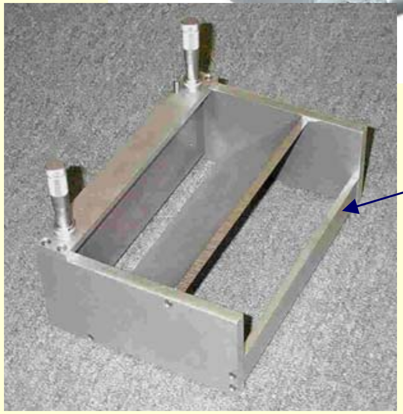
Laminate and burn out organics

Sinter

HIP







Doctor Blade Assembly

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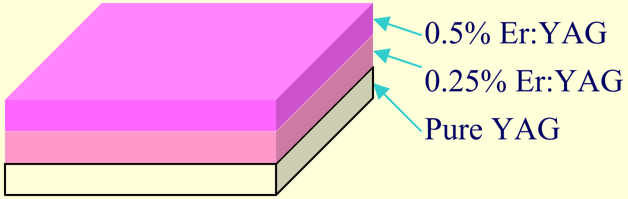
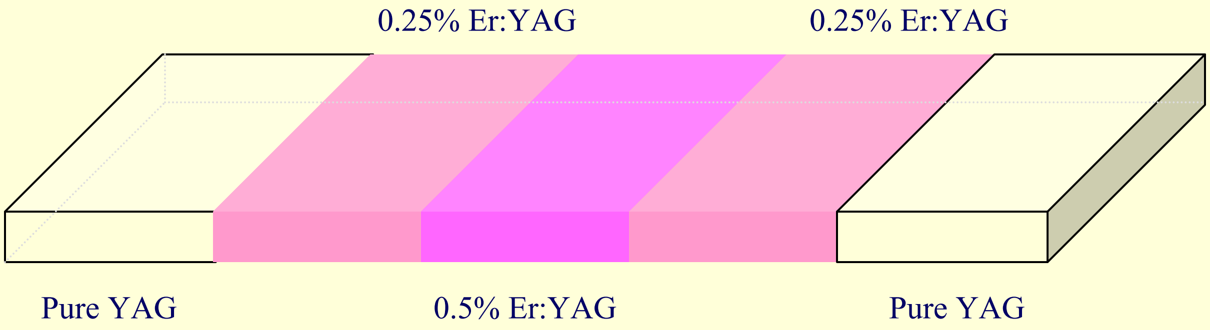
***Patent application filed (Method for Manufacture of Transparent Ceramics)**

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



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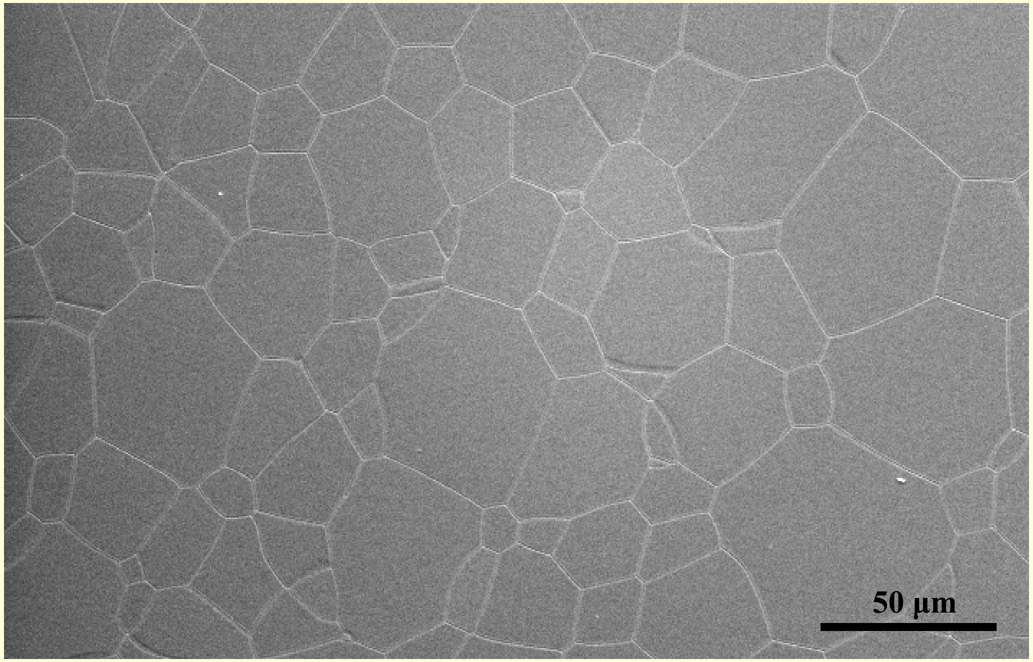
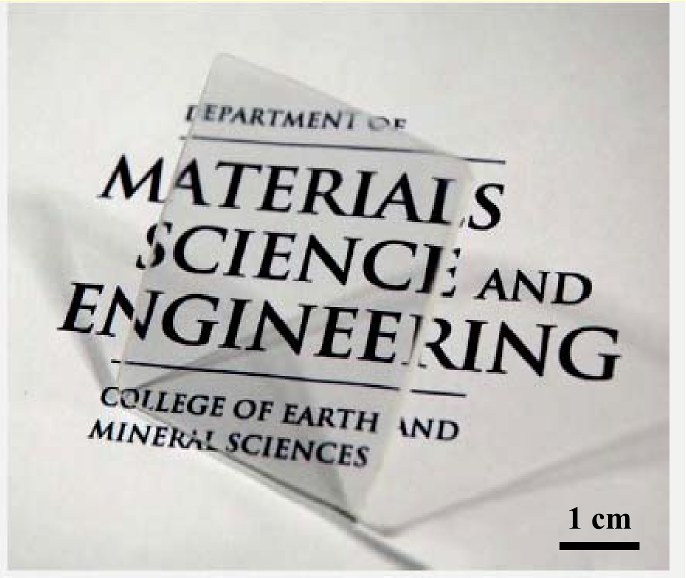
***Patent application filed (Method for Manufacture of Transparent Ceramics)**

Pure YAG part (45 x 45 x 3 mm)

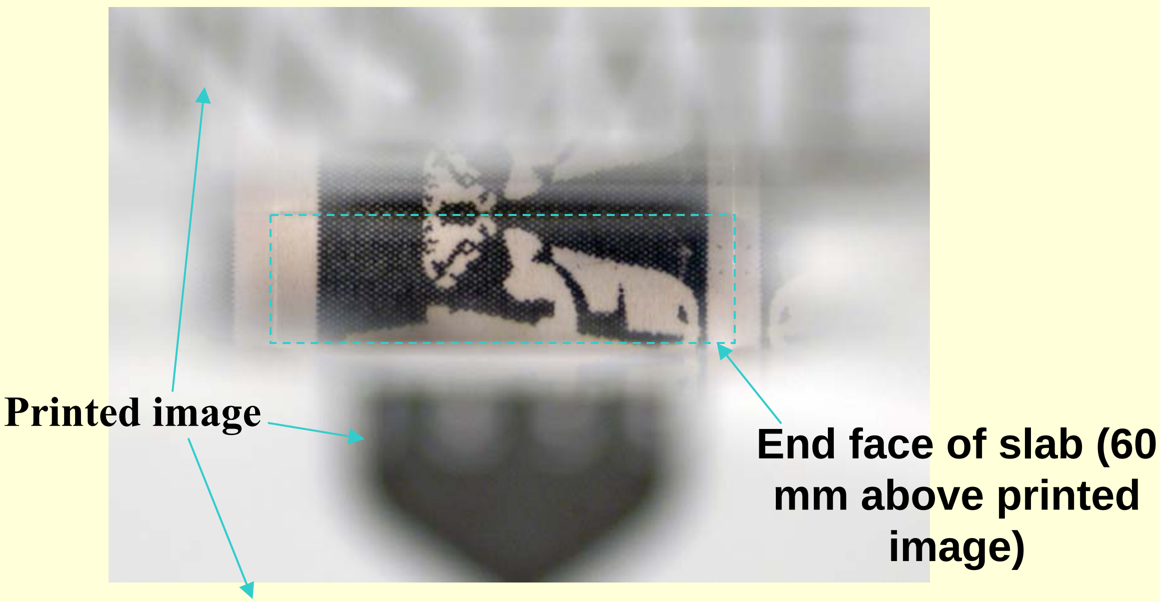


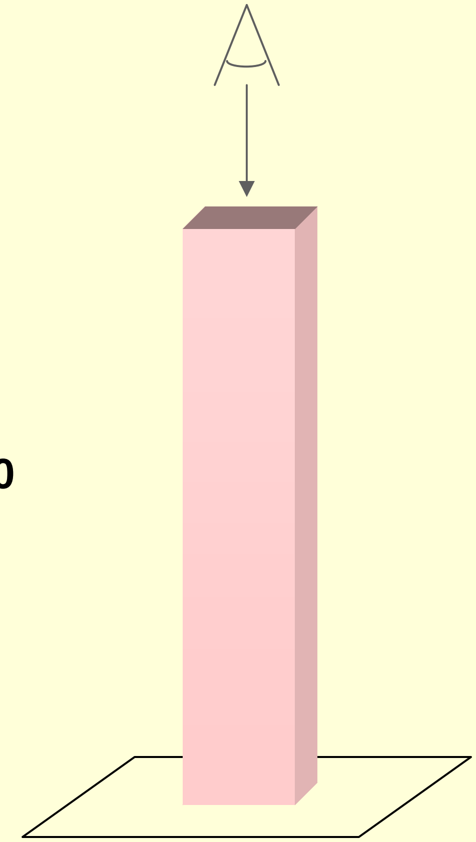


Sinter conditions: 1800°C/16 hr/vac

Visual transparency of a composite slab

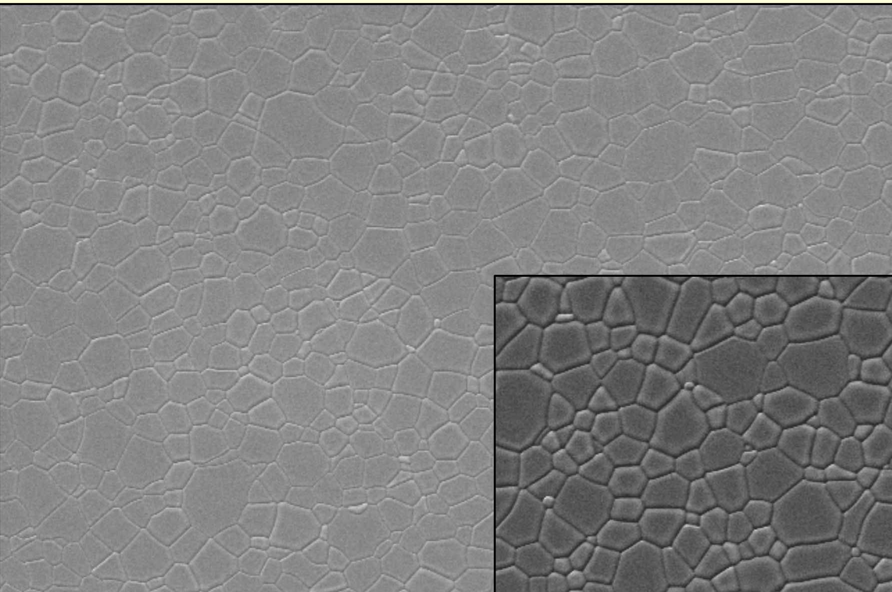
Photograph through the length of a 3.5 x 12 x 60 mm co-cast ceramic composite Er:YAG slab





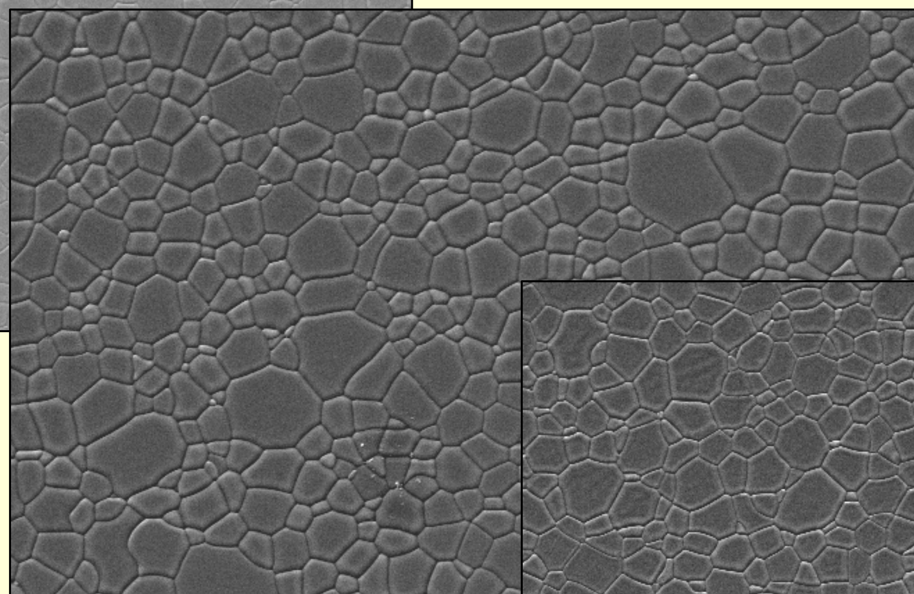
Er:YAG composite microstructure

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



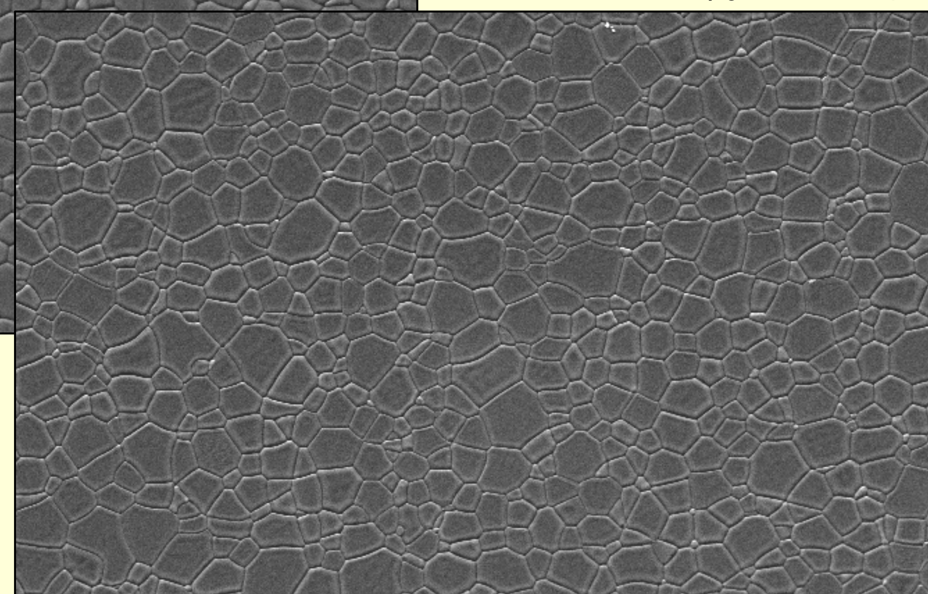
Pure YAG

0.25% Er:YAG



10 μm

0.5% Er:YAG



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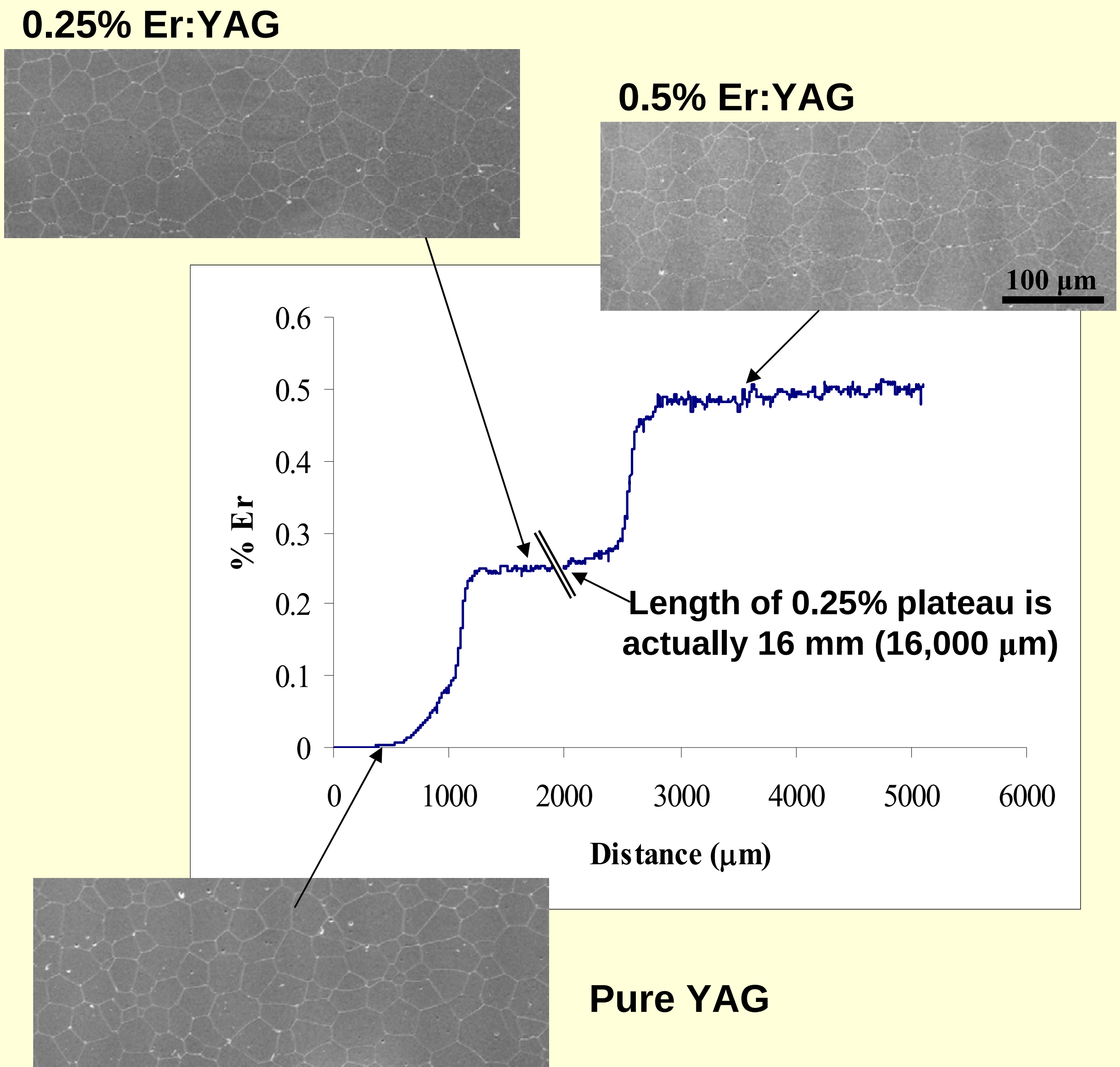
Er gradient across the co-cast composite



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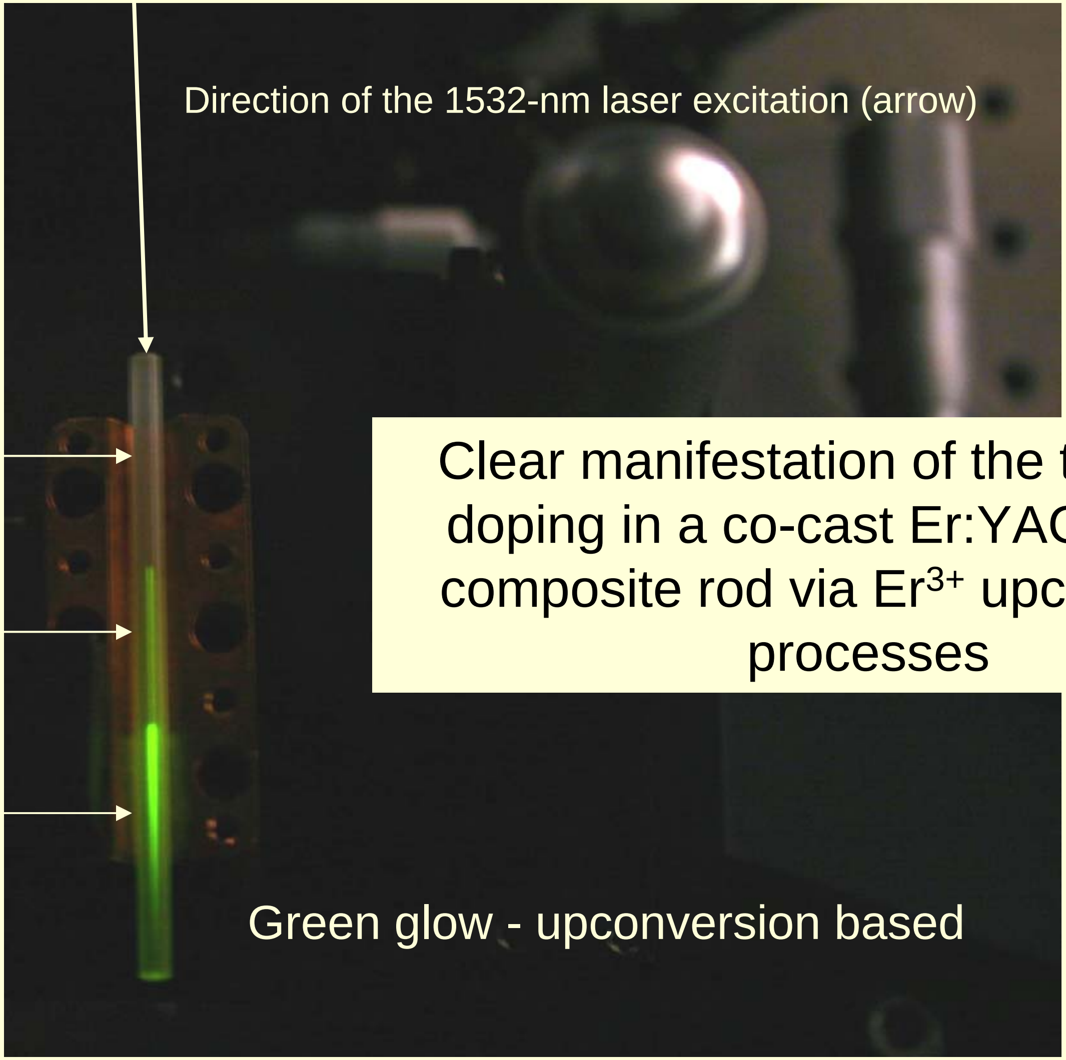
Visual Confirmation of the dopant concentration distribution in an Er:YAG composite rod

Pure YAG

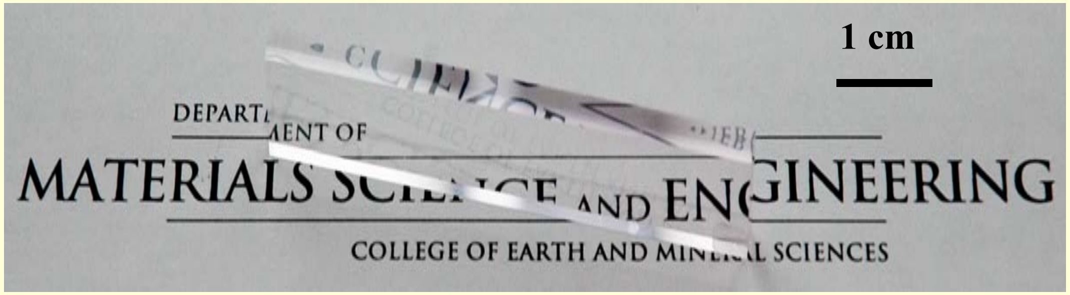
0.25 at% Er: YAG

0.5 at% Er: YAG



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

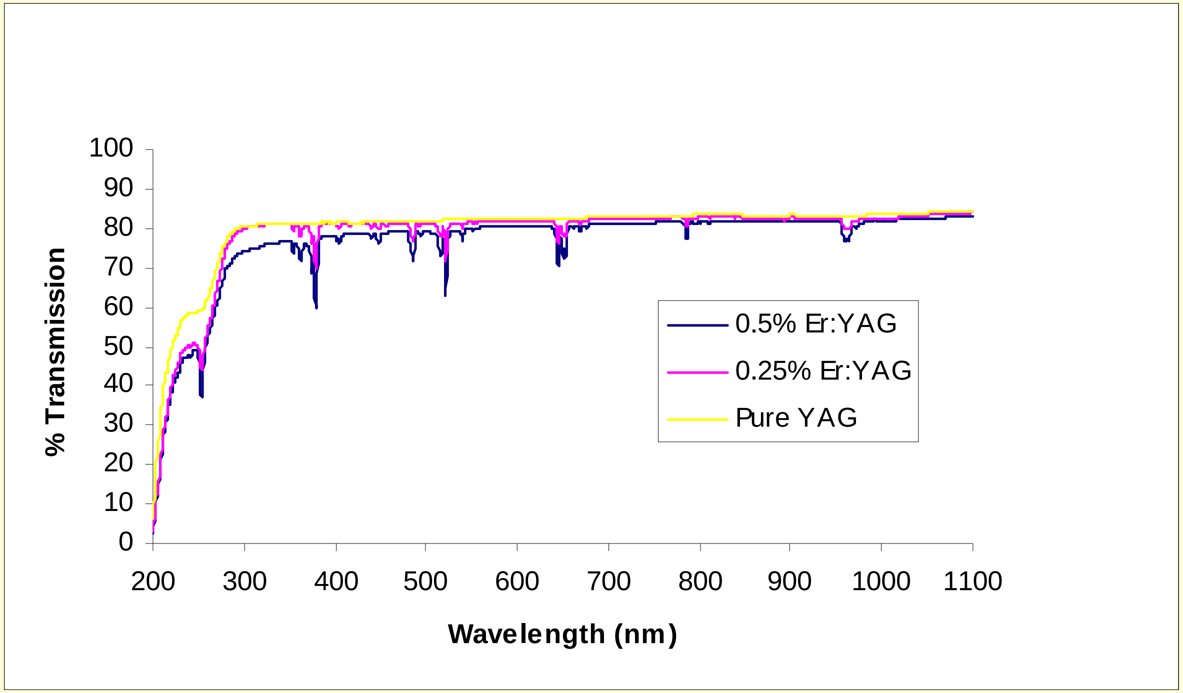
In-Line transmittance of a co-cast Er:YAG composite slab



At 1064 nm, transmittance is:

- Pure YAG – 84%
- 0.25% Er:YAG – 83.6%
- 0.5% Er:YAG – 82.7%

Theoretical transmittance (84%)



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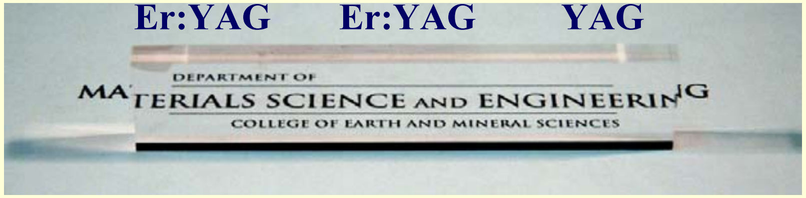
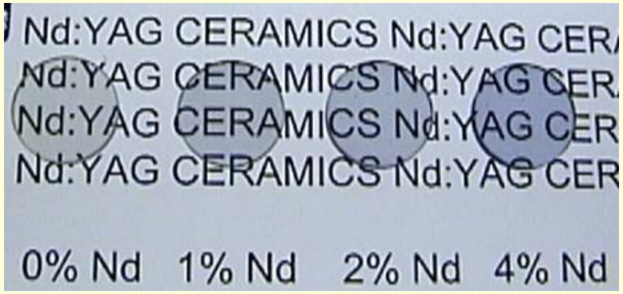
Transparent YAG ceramics developed at Penn State

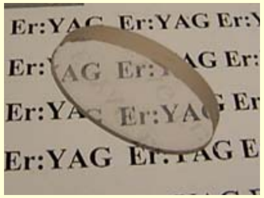
0.50% Er:YAG | 0.25% Er:YAG | Pure YAG



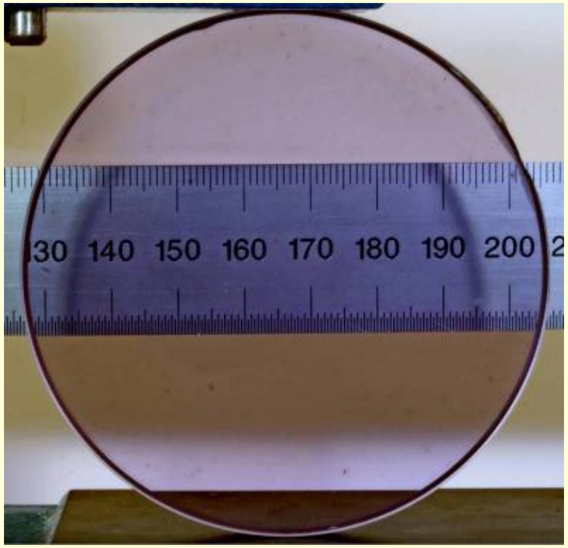
Segmented Er:YAG composite slab (tape cast), 12 x 60 x 3.5 mm



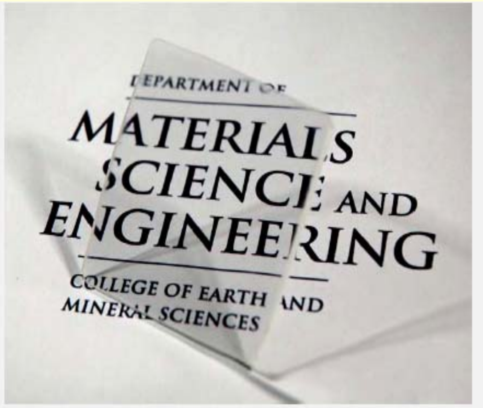
Nd:YAG (dry pressed) 22 mm ϕ x 3 mm thick



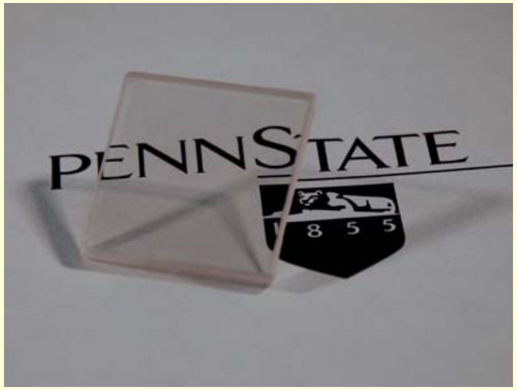
1% Er:YAG (dry pressed), 22 mm ϕ x 4 mm thick



1% Nd:YAG (slip cast), 78 mm ϕ x 5 mm thick



Pure YAG (tape cast), 45 x 45 x 3 mm



Stacked Er:YAG composite (tape cast), 25 x 25 x 3 mm (0/0.25/0.50% Er:YAG – bottom to top)

The Messing Group

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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

Project supported by *JTO Contract #FA9451-06-D-0012 and VLOC Inc and the* National Science Foundation Grant # DMR07-4931

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“Where did I put that screw?”

"It's in here somewhere"

"I think I've got it"

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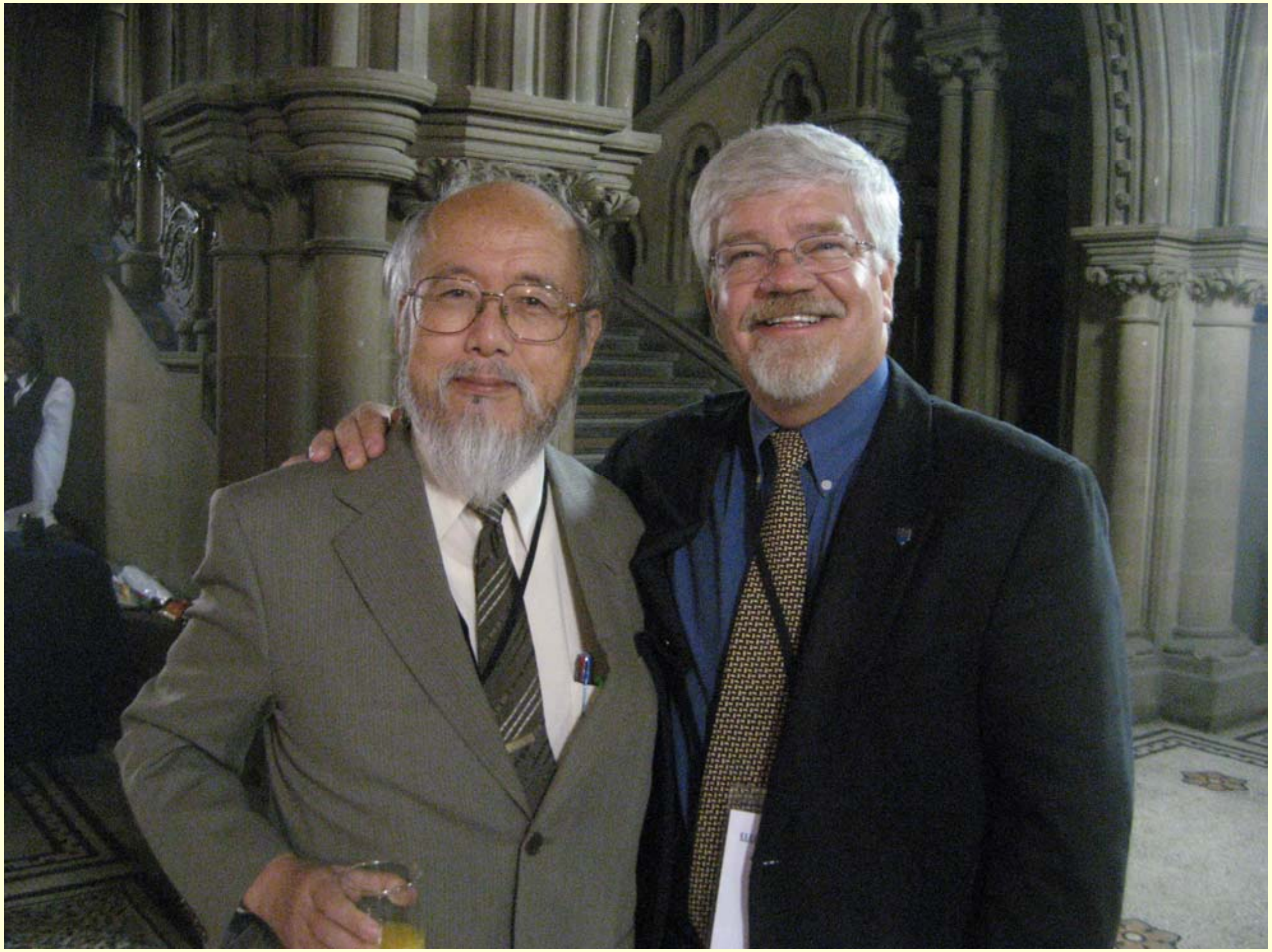
“Gary, Can you help me out of here?”

"Gary, That sweatshirt looks good on you"

Trying to look like Ludwig



Mapping the Rund Um course

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“The water is warm. Come on in!”

"Hang on!"

“Gary, Isn’t sailboat racing fun?”

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See, I told you this would be fun.

Thumbs up!

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Still smiling

Sailing without wind

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He does rest!

His pride and joy

Thank you Ludwig and Gisela

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1 8 5 5

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