Transparent ceramics for photonic applications

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Outline of my presentation

Introduction

Fabrication

Physical property (YAG LuAG)

Farady material(TGG)

Laser materials(mixed-garnet,squei-oxide)

Scintillator ceramic

Composite ceramic

Samary

Transparent ceramics for photonic applications

Since 1980's, we have been developing the transparent ceramics. Because ceramics have several advantages over single-crystal and optical glass. Our ceramics are widely used for lighting, laser, scintillator and many applications.

Arc-tubes for HID lamp

Single crystal

- Highly thermal & mechanical properties
- Expensive

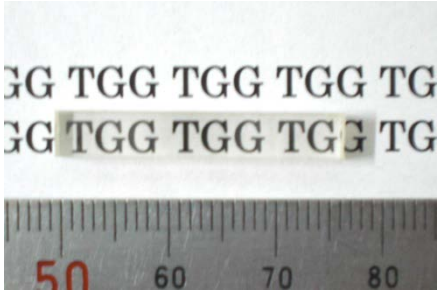
Optical glass

- Scalability, near-net shape
- Mass production

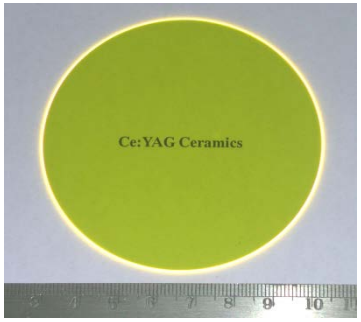
Transparent ceramics

Laser, Scintillator

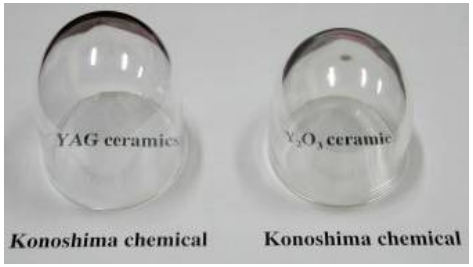
Lighting etc.



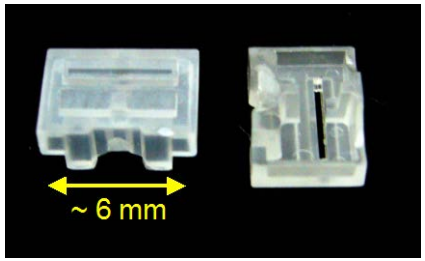
Faraday rotator



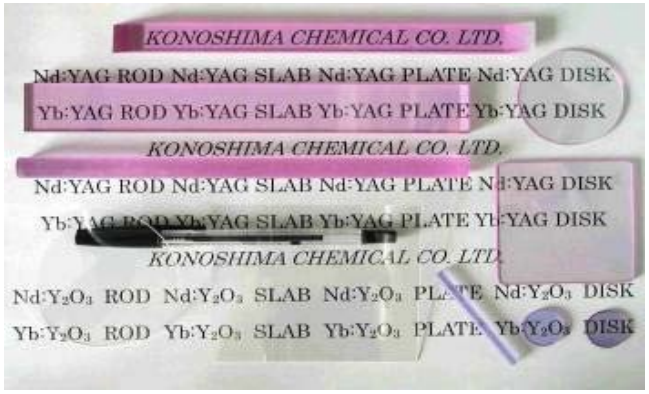
Scintillator & phosphor



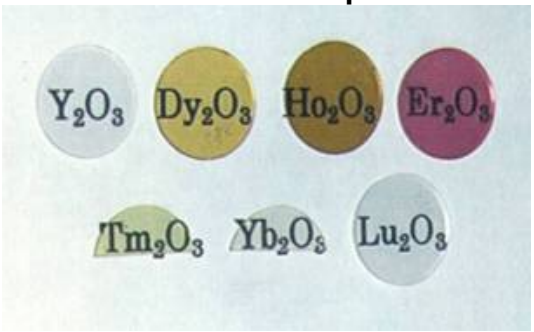
Infrared optics



Small part with complex structure



Window & Laser ceramics



Sesqui-oxide ceramics

Ceramic laser material

Transparent ceramic has several advantages over the single crystal laser material

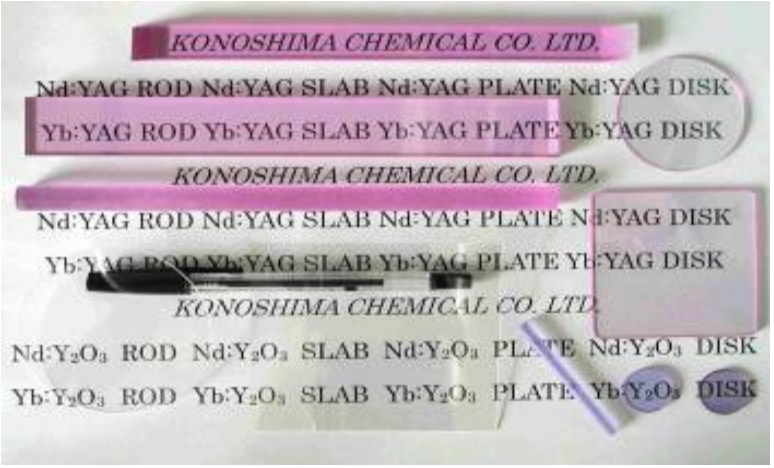
Property Comparisons

Property	Ceramic vs. Single Crystal
• Thermo-Optic Coefficients	Identical
• Spectroscopic Properties	Identical
• Solarization (lamp-pumped)	***Ceramic inferior***
• Diode-Pumped Performance	Nearly - identical
• Wave-Front Distortion	**Ceramic superior**
• Bonding Ease/Cost	**Ceramic superior**
• Scatter Loss	**Ceramic comparable**
• Stress Fracture	***Ceramic slightly superior***
• Dopant Gradient	**Ceramic superior**

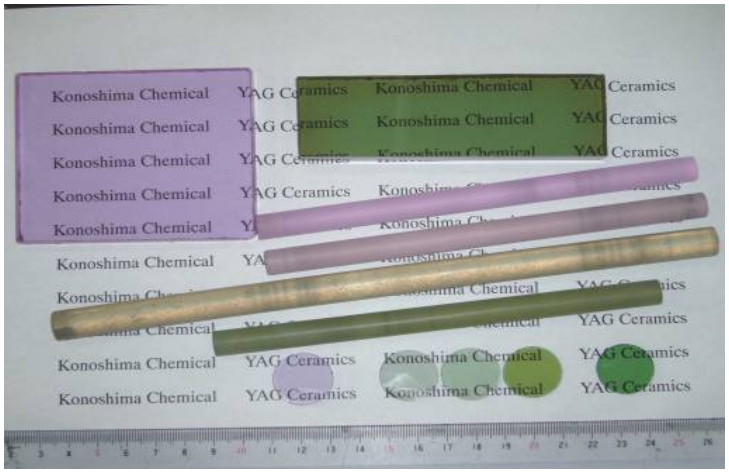
Ref. Gregory J.Quarles: Paper IO-C11 3rd Laser ceramic symposium, 2007

YAG laser ceramics

YAG is the most important laser material. We have been fabricating the YAG laser ceramics as for commercial products



Nd:YAG slab & disk



Cr/Nd:YAG for solar pumped laser

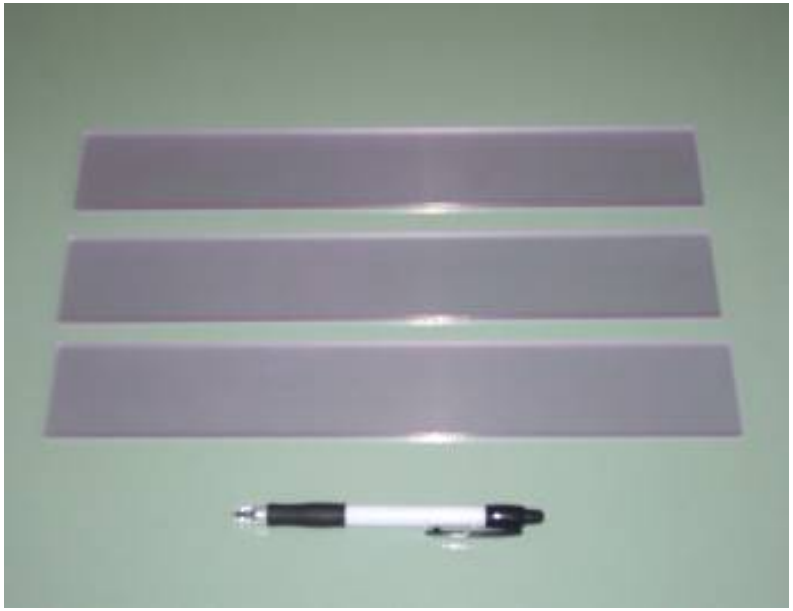
Er:YAG, Ho/Tm:YAG for eye-safe laser

Yb:YAG with large aperture

composite ceramics

Large-scale Nd:YAG Ceramics (the current state)

The large-scale laser materials are necessary for high-power laser systems. Unfortunately, the size of single-crystal is limited.But recently, it is possible to fabricate the large-scale laser materials by using ceramic technology.



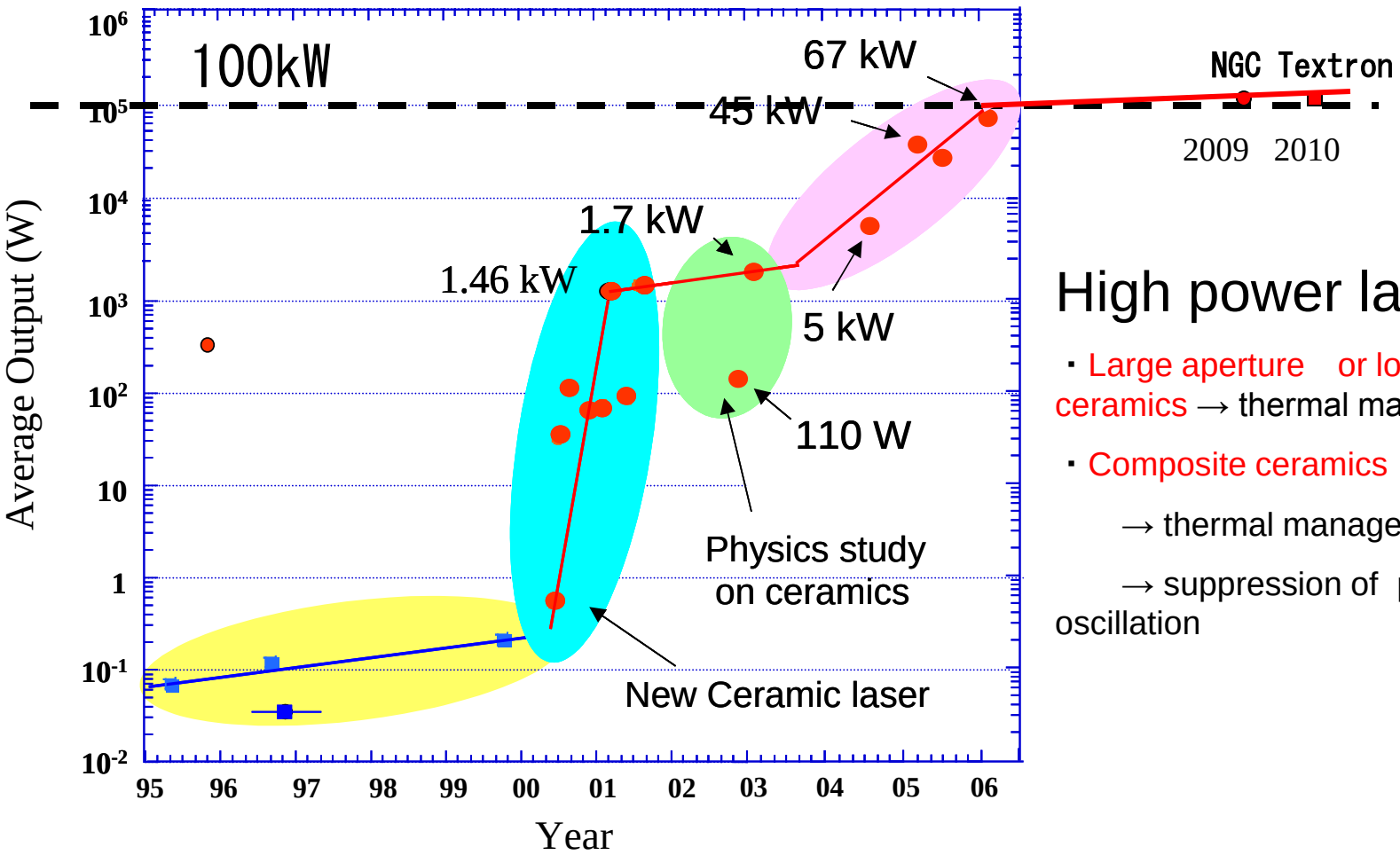
Disks with large aperture

10 ×10 ×2 cm

Slabs with long length

~ 35 cm

Recent progress of Nd:YAG ceramic lasers



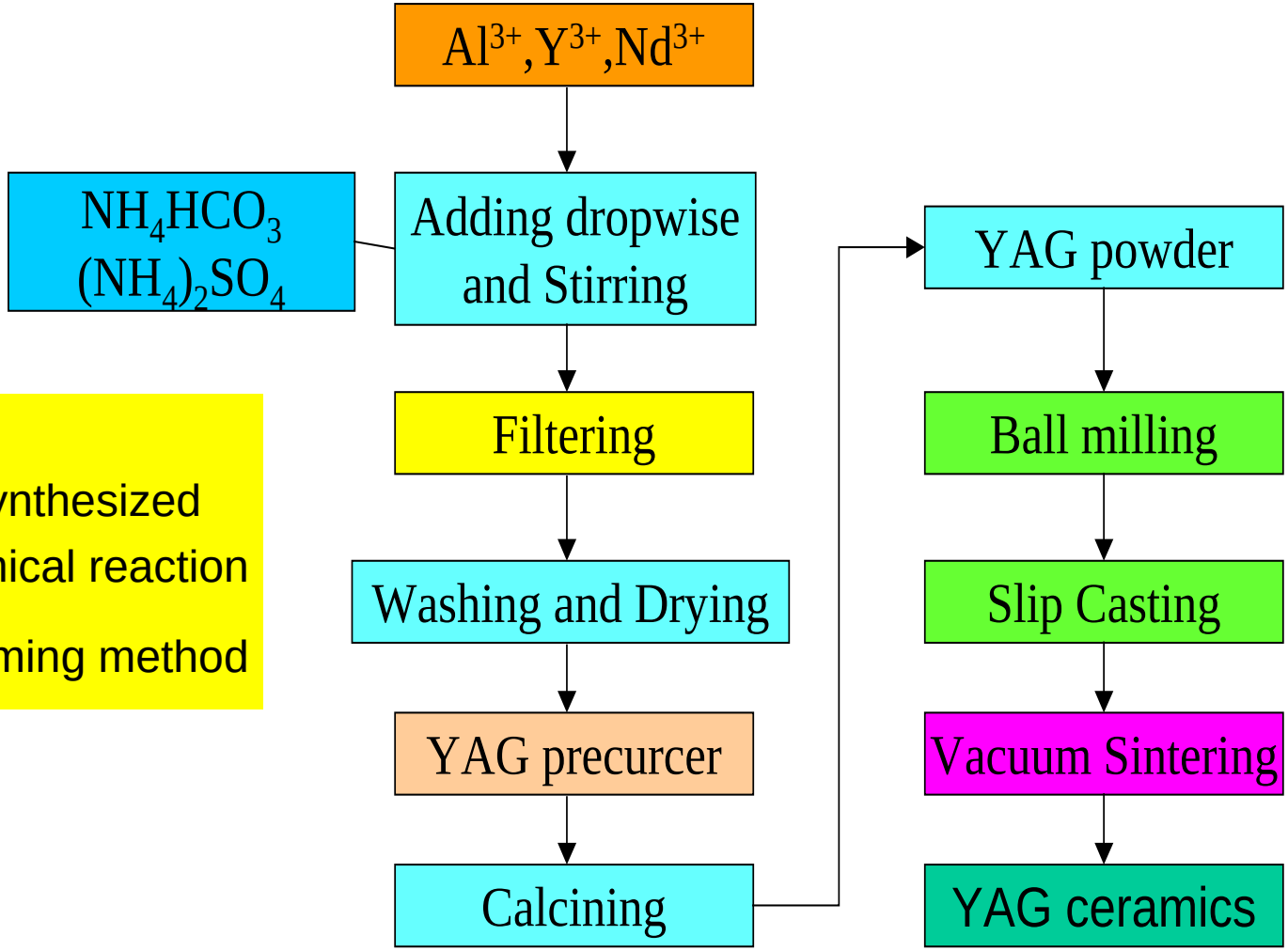
High power laser

- Large aperture or long ceramics → thermal management
- Composite ceramics

  → thermal management

  → suppression of parasitic oscillation

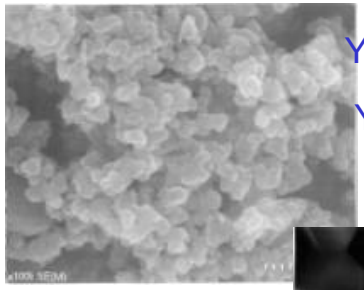
Fabrication flow of YAG Ceramics



Key technologies

- Powder is synthesized by wet chemical reaction
- Slip cast forming method

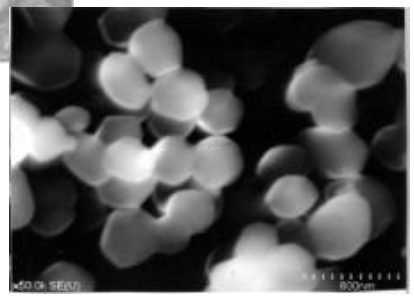
Fabrication of YAG Ceramics



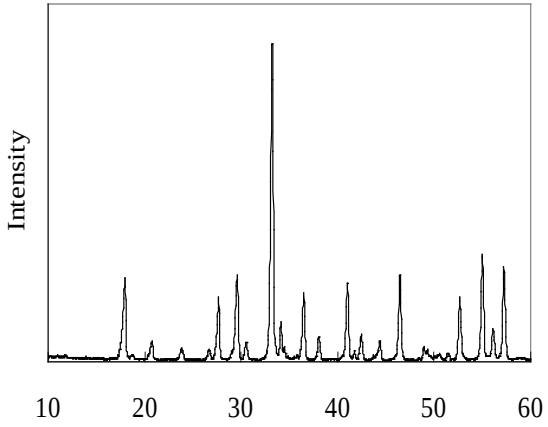
YAG Precursor ~nm order

$Y,Al(OH)_3,Y,Al(CO_3)_3$

Calcining
~1200 ° C

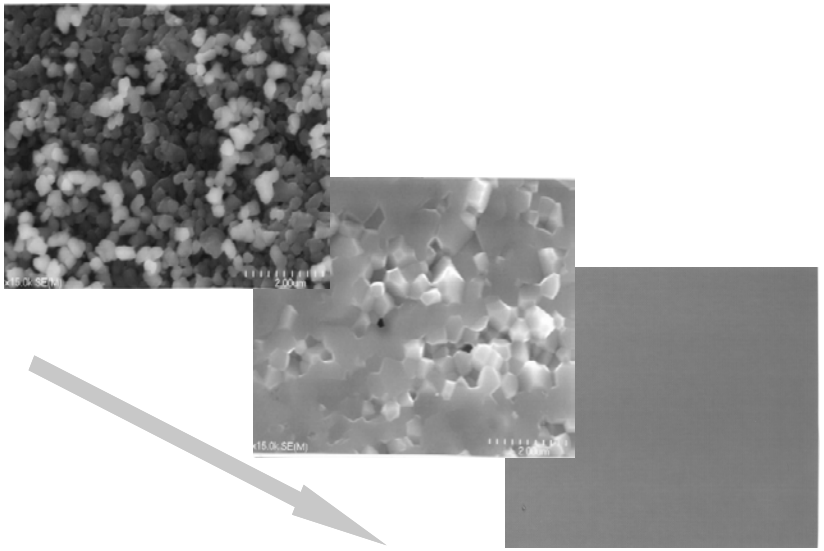


$Y_3Al_5O_{12}$ high purity powder
~submicron order



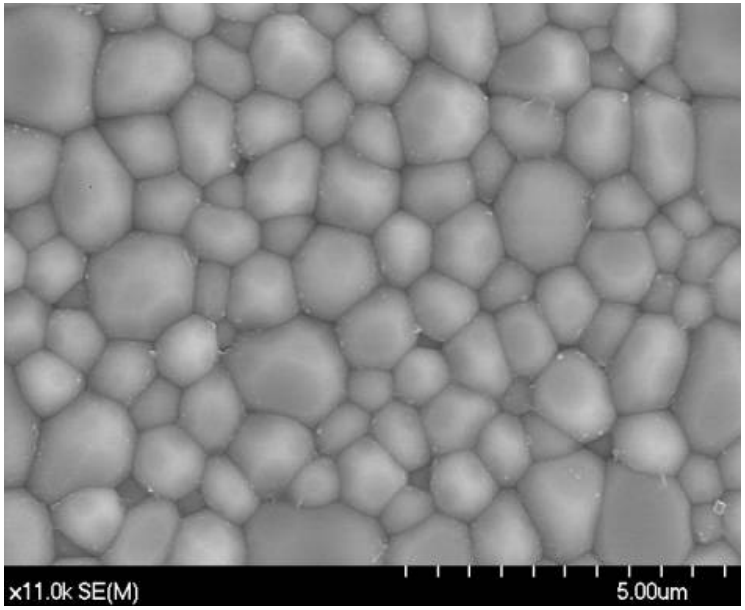
XRD pattern of the YAG powder

Inside of the green body
(density > 60 %)

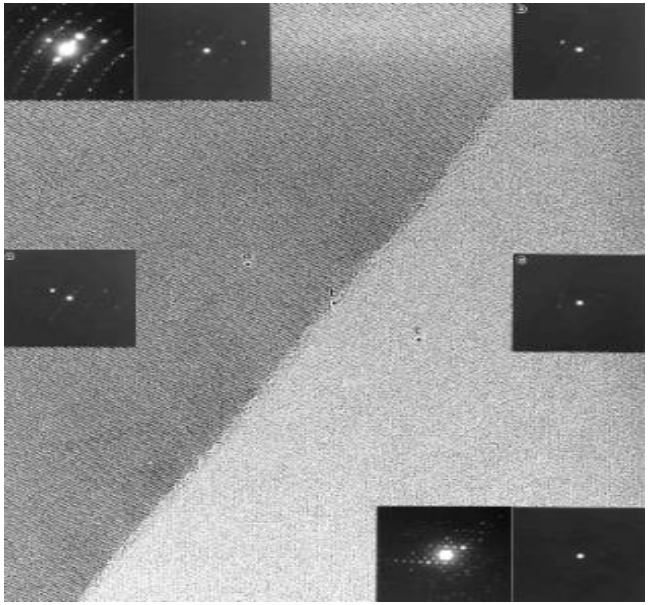


After sintering, pore free structure was obtained

Microstructure of YAG ceramics



SEM image



TEM image of grain boundary

The average grain size of our ceramic is about 3 μm in diameter.

The width of grain boundary is very narrow

Benefits of fine grain

The grain size of our ceramic is relatively small. Ceramic with fine grain have two advantages:

Fracture strength (σ) of ceramics decreases in the inverse proportion to the grain size

$$\sigma = \sigma_\infty + \sigma_1 D^{-1/2} \quad (1)$$

or

$$\sigma = \sigma_1 D^{-\alpha} \quad (2)$$

σ_∞, σ_1 : constant

D : average grain size

Local depolarization (P_Γ) of ceramics increases in proportion to the grain size

$$P_\Gamma \sim p^2 D T^{-1} \quad (1)$$

P : radiation power

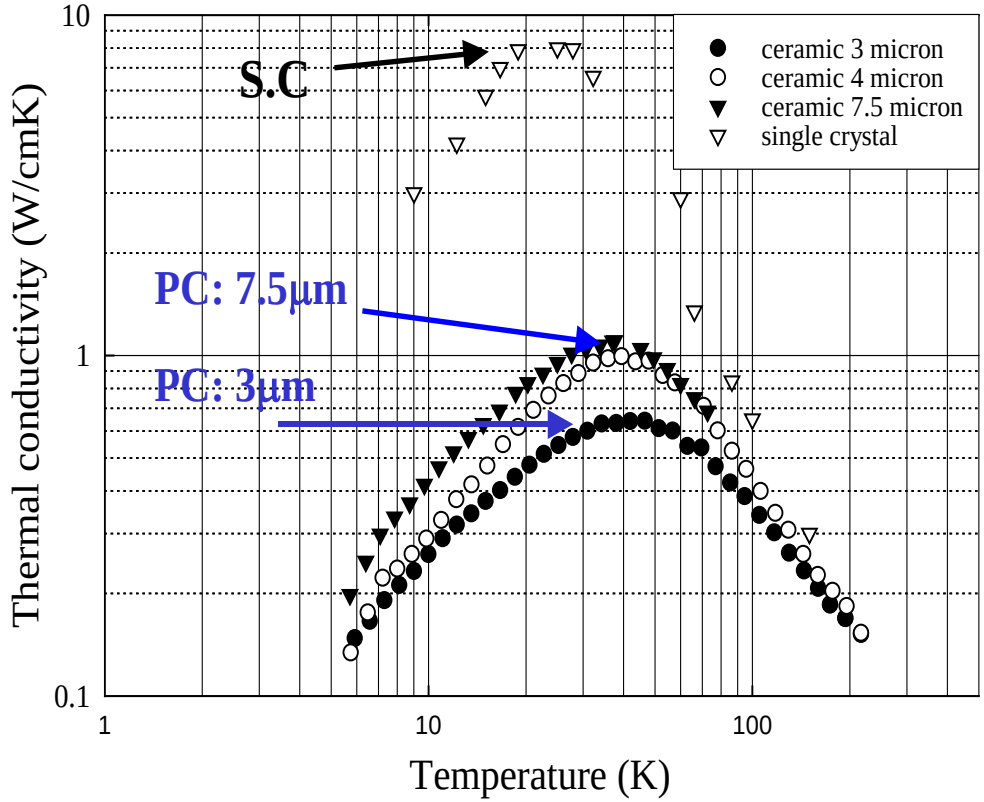
D : average grain size

T : optical pass length

M.A.Kagan, E.A.Khazanov: Quantum Electronics 33(10) 876-882 (2003)

Thermal conductivity

The thermal conductivity of YAG single-crystal and ceramic with different grain size at low temperature



H. Yagi et al. Ceramics International. Vol.33, 711-714(2007)

Thermal conductivity of 1%Nd:YAG at R.T (20°C)	(W/mK)	
Single-crystal	10.5	(our work)
Ceramics	10.7	(our work)
Single-crystal	9.3	(Ref.1)
Ceramics	8.7	(Ref.1)

Ref.1: Technical leaflet of VLOC

At low temperature, thermal conductivity of ceramic is lower than that of single-crystal, because the phonon mean free path becomes longer, and phonon scattering occurs at the grain surface

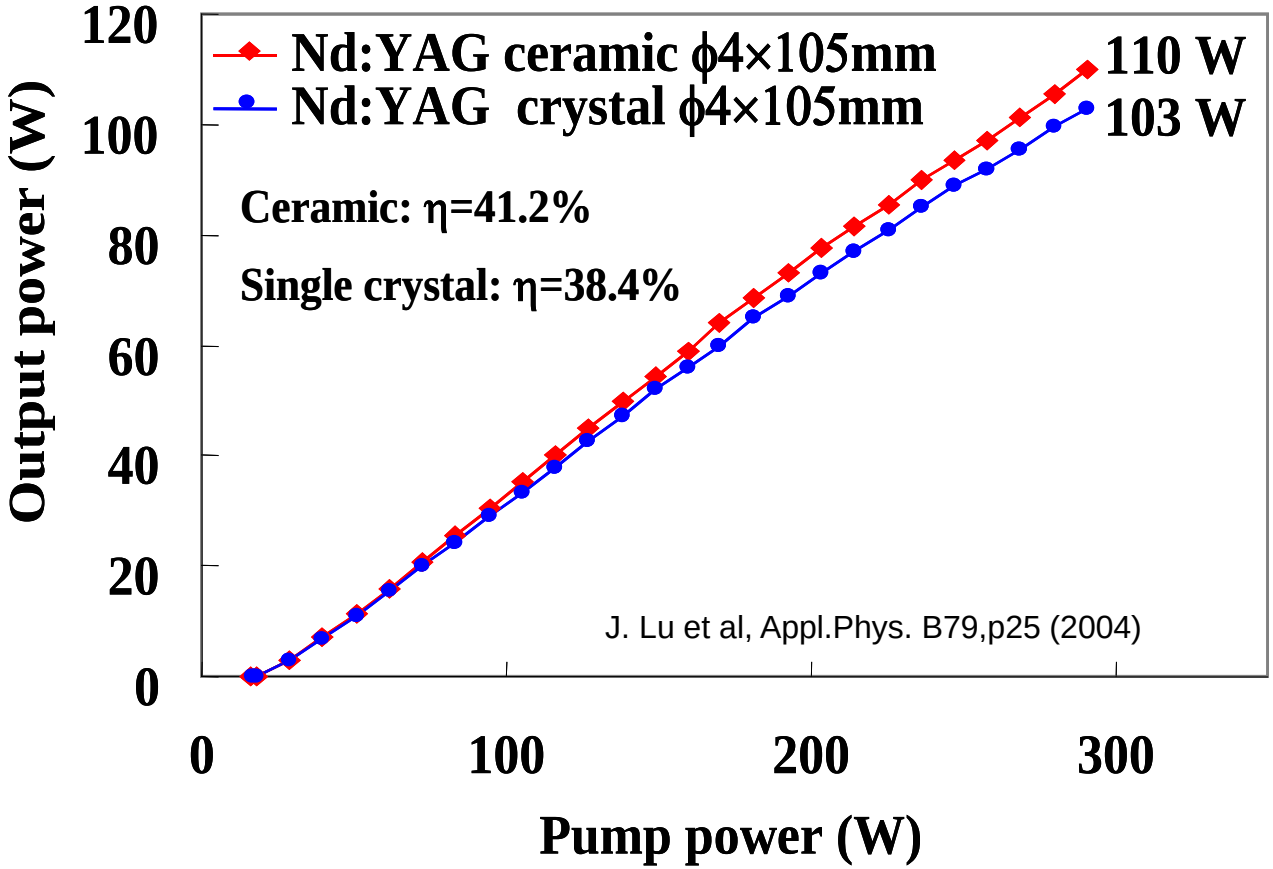
Physical properties of YAG ceramics

■Young's modulus	308 GPa
■Poison ratio	0.23
■Fracture strength	370 MPa
■Fracture toughness	5.4 $MPam^{1/2}$
■Thermal expansion coefficient	8×10^{-6}
■Thermal conductivity	11.7W／(m･℃)
■Specific Heat	0.590J／(g･℃)
■Hardness (Hv)	15 GPa
■Refractive index at 590nm	1.825
■Density	4.55g／cm^3

The ceramic is about 15% harder and the fracture toughness is up to 3 times higher than that of single crystal.

Other physical constants are almost the same as the single crystal.

We demonstrated high power ceramic laser (2004)

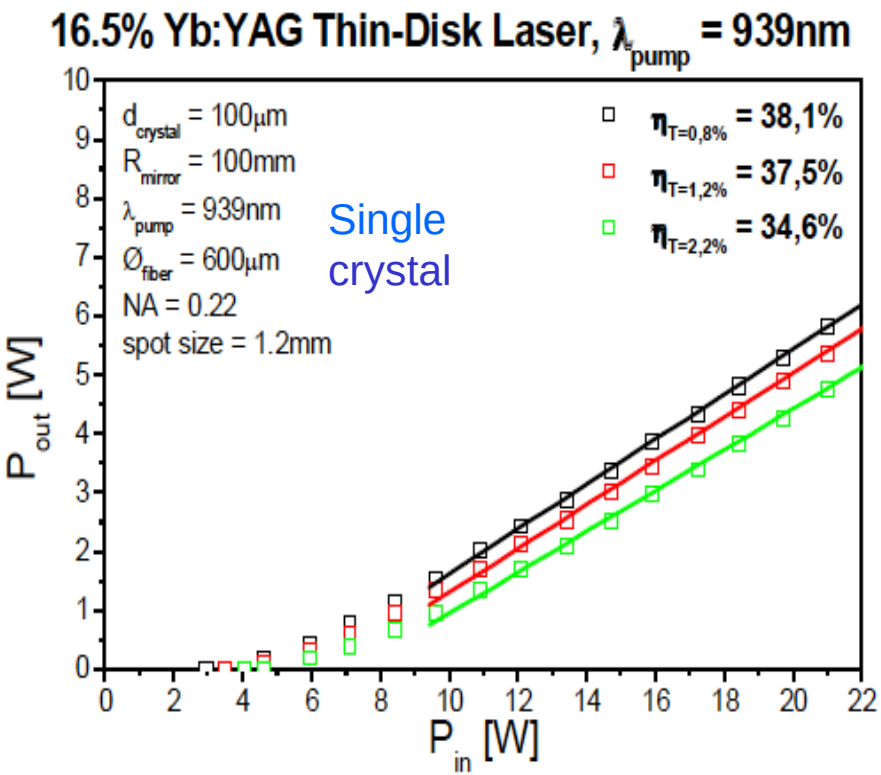


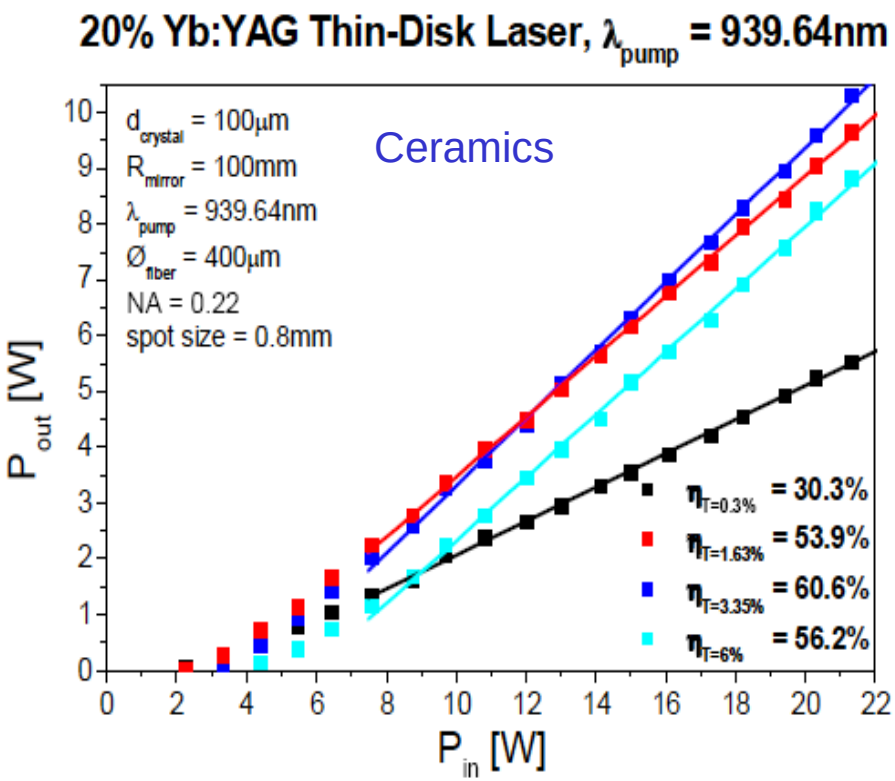
High power Nd:YAG ceramic laser reached the same level or even higher in efficiency with Nd:YAG single crystal laser.
As a result, we showed the possibility of transparent ceramics for laser material.

Highly doped Yb:YAG thin-disk laser

Ytterbium ions doped laser material is attractive to the high power, high energy, because of lower quantum defect.

Thin-Disk Laser Experiments (24 pump passes)





Yb:YAG ceramics achieves over 60% slope efficiency

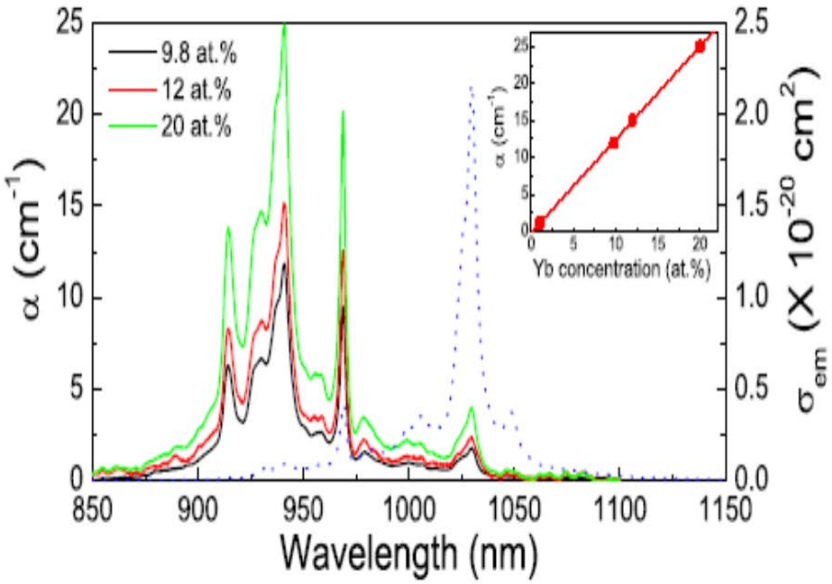
S.T.Fredrich-Thornton, et al, WB13, Advanced Solid-State Photonics 2008

Yb:YAG

Ytterbium ions doped laser material is attractive to high power, high energy, because of lower quantum defect.

Application: High-power thin-disk laser, Fusion driver etc

Absorption and emission spectra of Yb:YAG ceramics at R.T



Yb:YAG ceramic disk

$Yb:Lu_3Al_5O_{12}$(LuAG)

The Yb:YAG is widely used for the high power laser applications because it has a large thermal conductivity. However, it was found that as the doping concentration of Yb is increased, the thermal conductivity of the Yb:YAG drops significantly.

The pursuit of efficient high power lasers with high beam quality has led to the development of the thin disc or micro-chip laser setup. In these laser setup, high Yb concentrations are needed to allow for sufficient absorption within the active medium.

Recently as what is replaced with Yb:YAG, Yb:LuAG attracts attention.

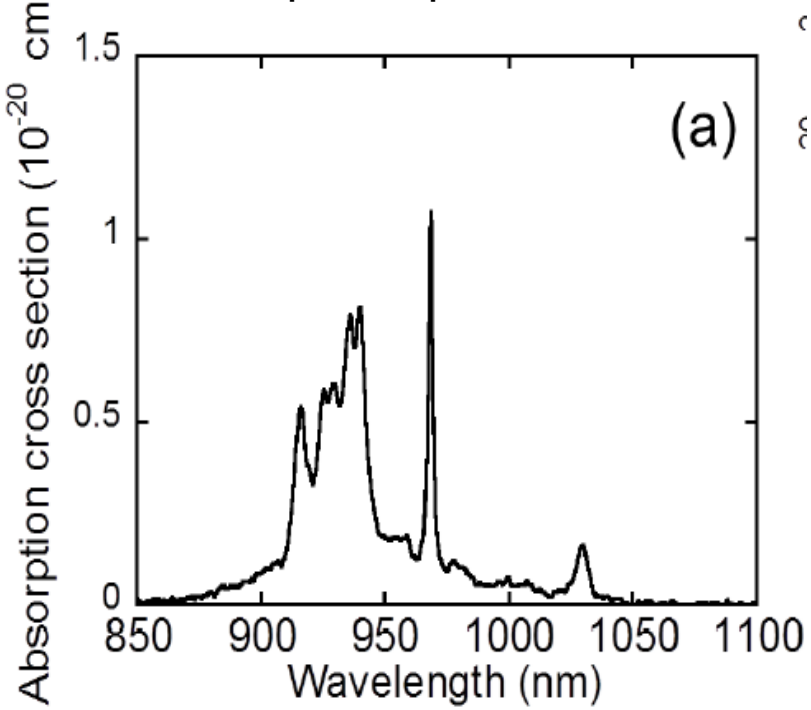
Table 1. Thermal Properties of LuAG and Yb:LuAG Ceramics and Single Crystals

	α (mm^2/s)	C_p (J/gK)	ρ (g/cm^3)	K (W/mK)
LuAG ceramic	2.44 ± 0.02	0.54	6.65 ± 0.07	8.80 ± 0.06
10 at.% Yb:LuAG ceramic	2.59 ± 0.07	0.47	6.67 ± 0.07	8.04 ± 0.03
LuAG single crystal				7.7 [9]
10 at.% Yb:LuAG single crystal				7.4 [9]

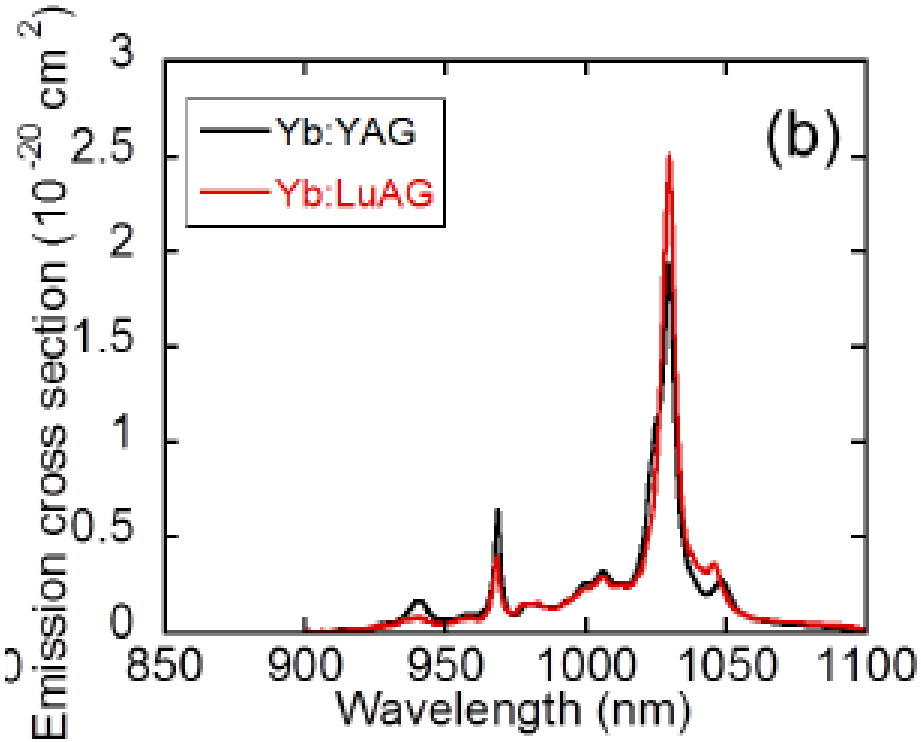
A.Shirakawa (2012)Vol.20,No14OPTICSEXPRESS15387

10%Yb:LuAG Ceramic

Absorption spectrum



Emission cross section spectra



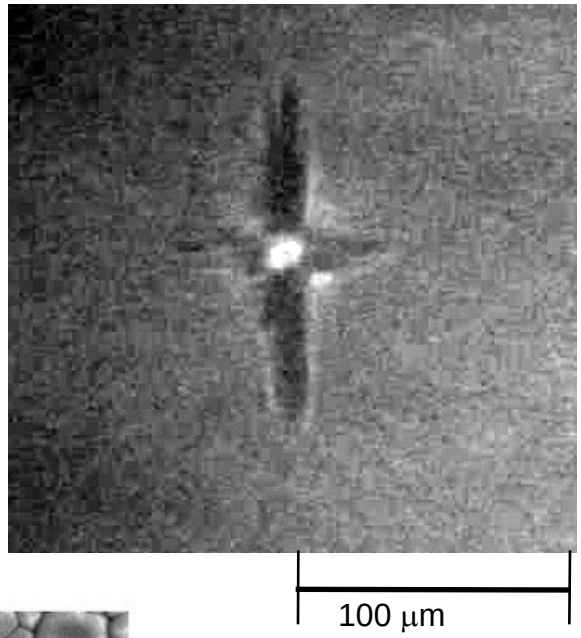
Zeroline:$_{\delta}\delta_{abs}$ =1.07 × 10^{-20}cm^2)and the second highest peak is around the 940nm absorption is very broad and suitablefor LDpumping Theluminence lifetime is 1.07ms .

Yb:LuAG has luminesence peaks at 1030nm(δ_{em}=2.0 × 10^{-20} cm^2). The FWHM of the main peak is 6.1nm The peak emision cross section of Yb:LuAG is 25% higher than that of Yb:YAG (δ_{em}=2.0 × 10^{-20} cm^2)

A.Shirakawa (2012)Vol.20,No14OPTICSEXPRESS15387

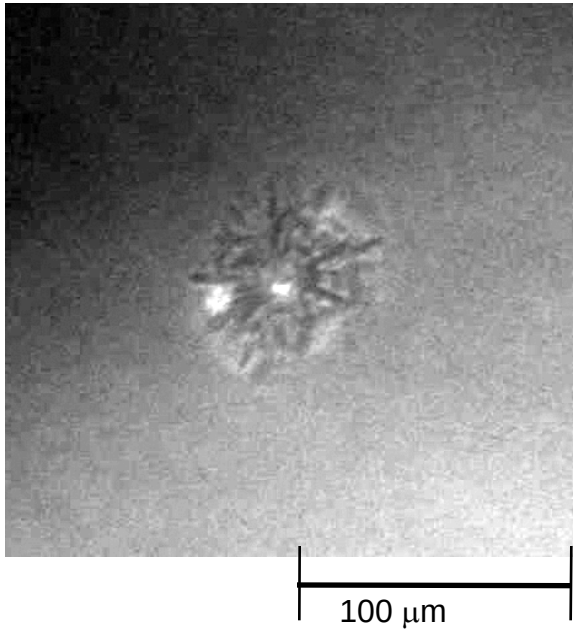
Damaged crack figures of (a) TGG single crystal and (b) TGG ceramic.

Single crystal TGG

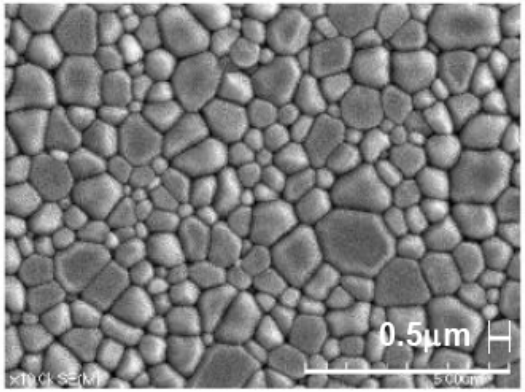


(a)

Ceramic TGG



(b)

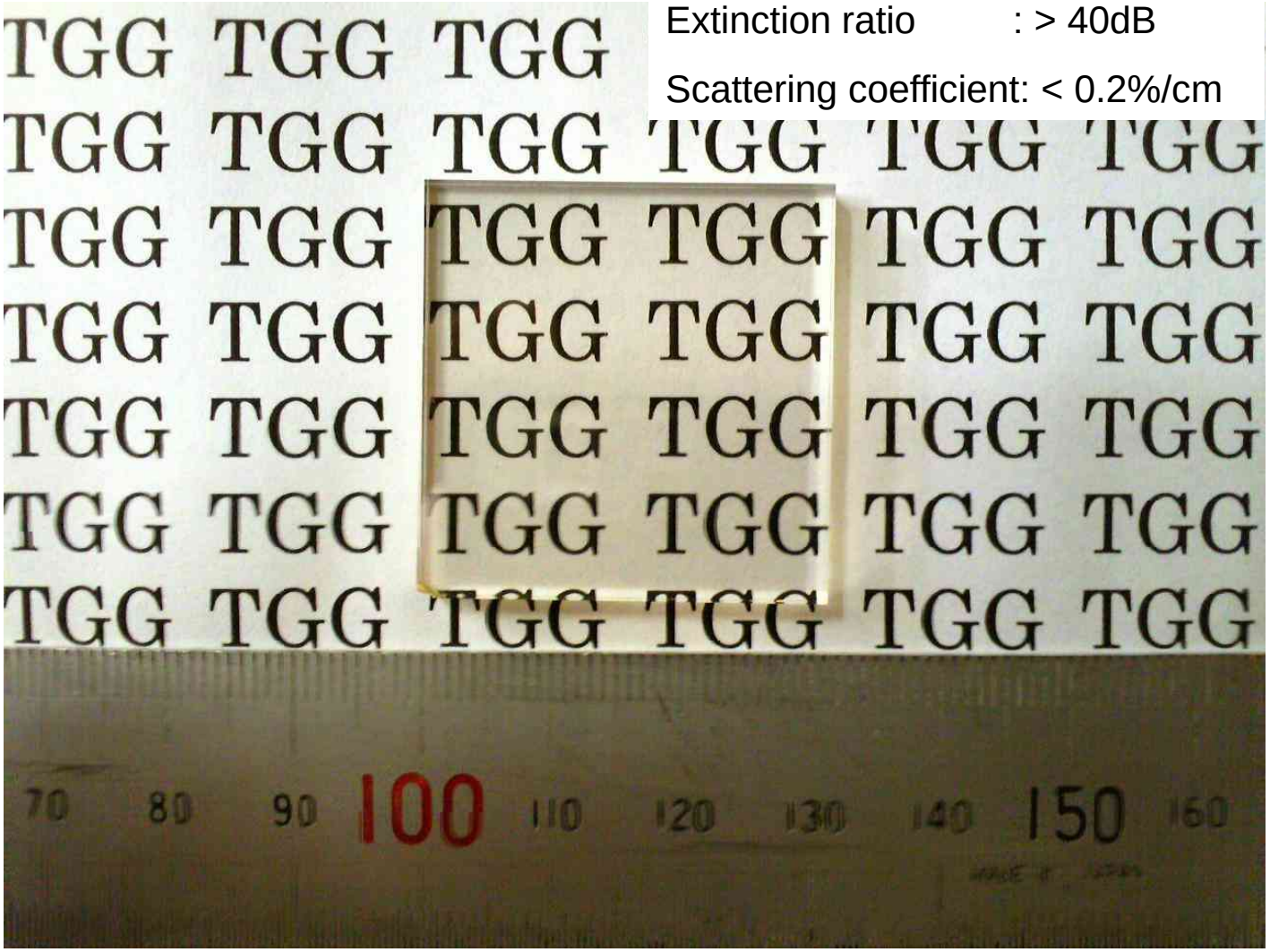


5μm

Microstrure of TGG ceramic

TGG ceramic

Faraday rotator is key devise of fiber laser or high peak power laser systems. TGG ceramics is an attractive material for Faraday element



Extinction ratio : > 40dB

Scattering coefficient: < 0.2%/cm

Faraday effect of TGG

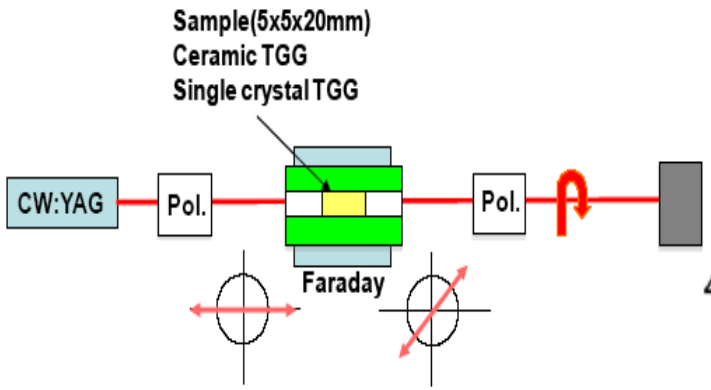
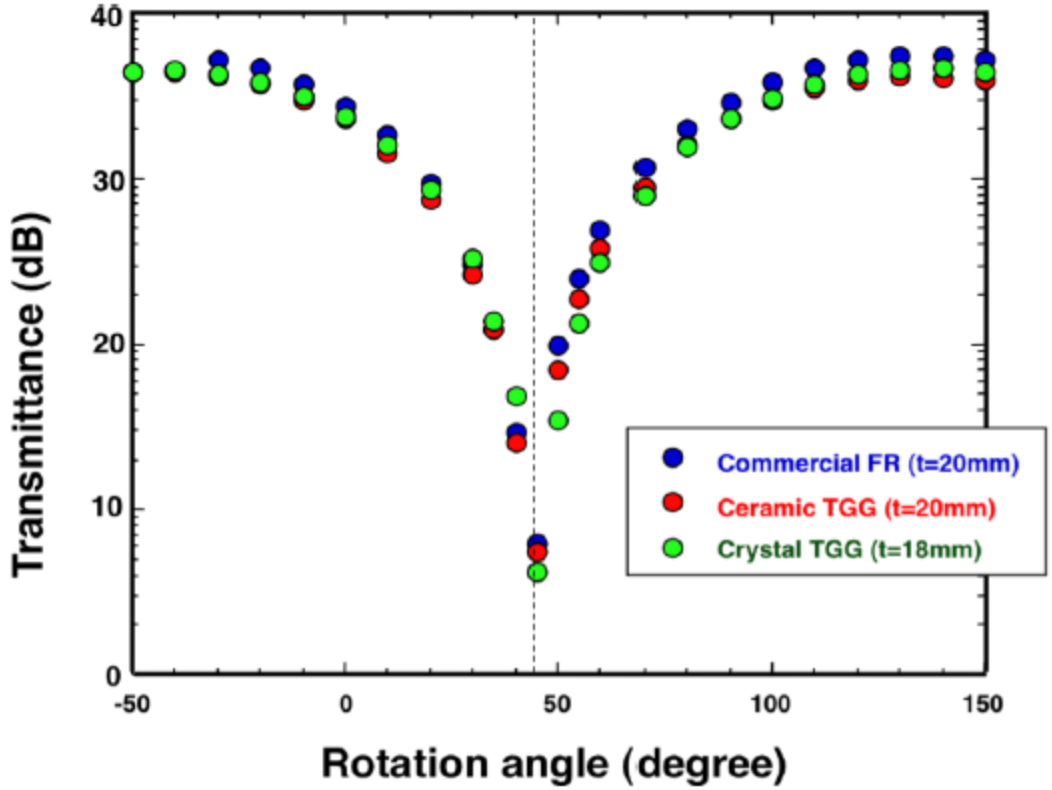


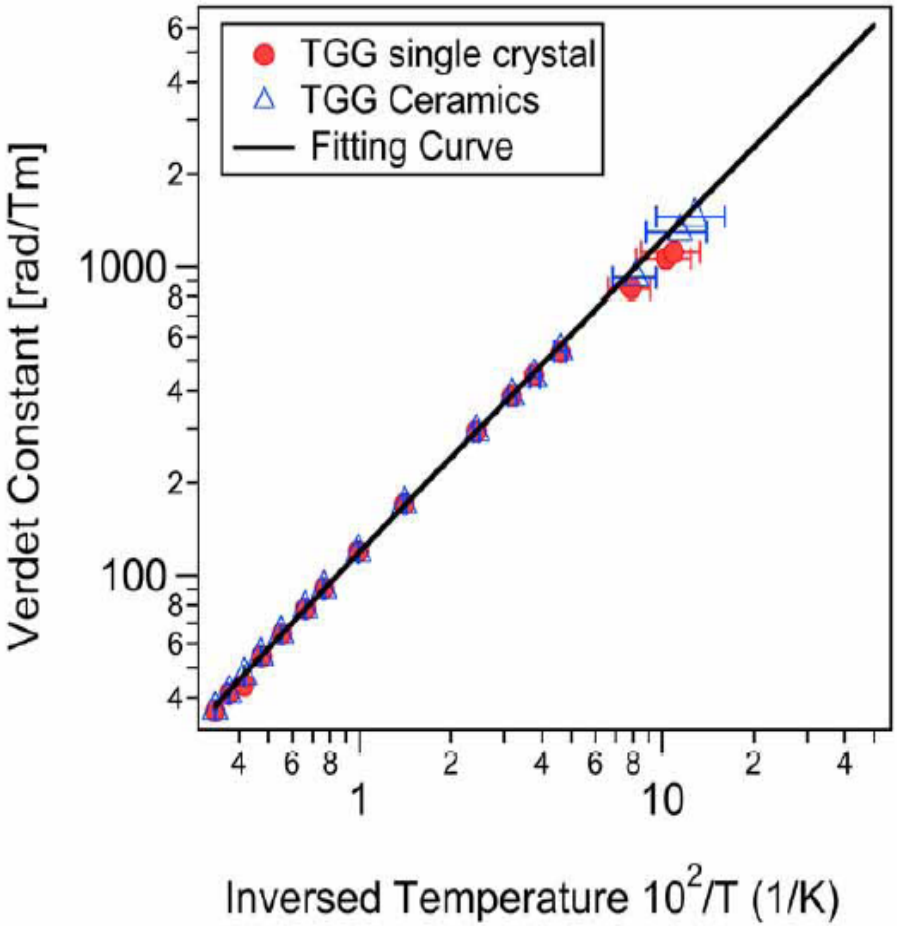
Fig. 4. Schematic showing the experimental setup for investigating TGG Fa

Farady effect of TGG



H.Yoshida,2011/vol19no16/OPTICSEPRESS 15183

Temature dependence of Vedet const of TGG ceramics,single crystal.



- thermalconductivity ~ 7 W/mK
- scalability

Verdet const.	single	ceramics
rad/Tm @R.T	36.4	36.2

Verdet constant of TGG ceramic is almost same as the single crystal

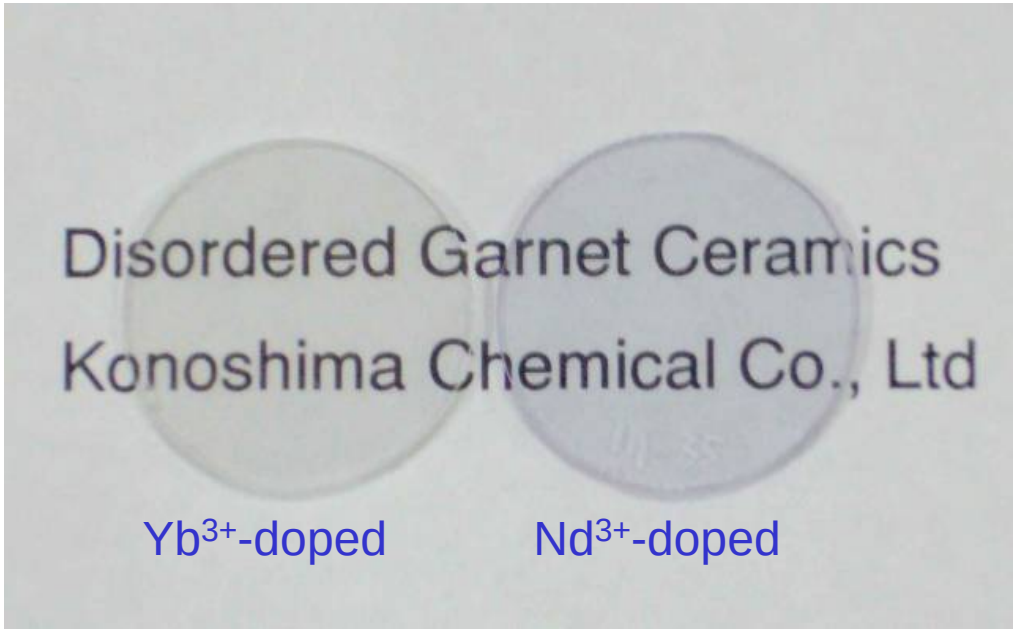
R.Yasuhara Optics Express vol.15, 11255(2007)

Mixed garnet ceramics

Nd^{3+}-doped mixed scandium garnets single crystal {(YGd)Sc(GaAl)O_{12}} and its mode-locked operation was reported by E. Sorokin *et. al*

J.Opt.Soc.Am.B **10**, 1436, (1993)

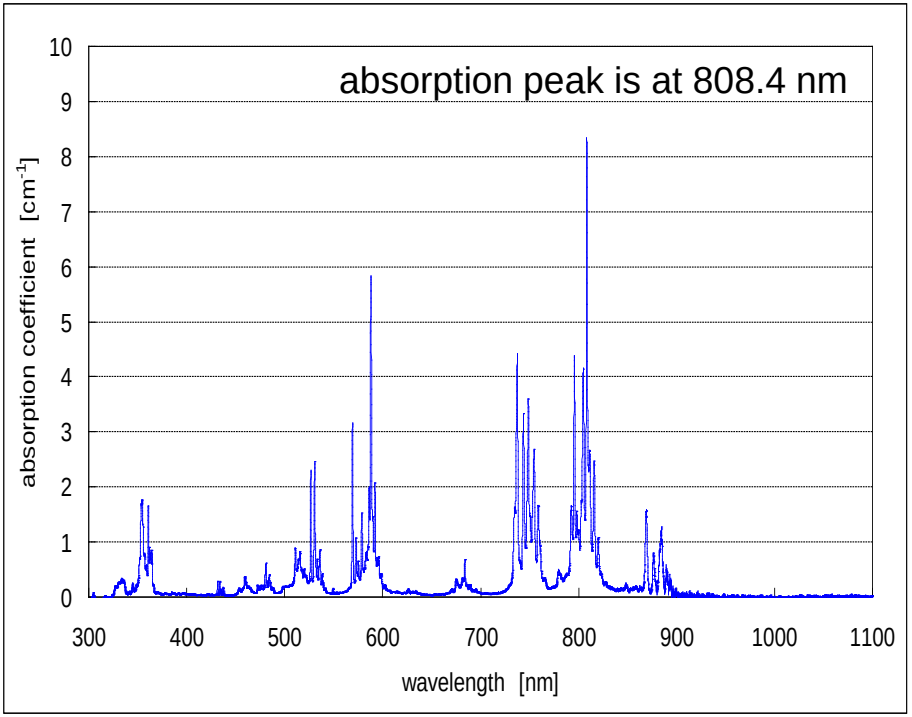
Mixed garnet with broad band spectrum is a candidate for short pulse laser gain material.
We had succeeded in fabrication of mixed garnet ceramics



{Gd_2Y}Sc_2{Al_2Ga}O_{12} ceramics

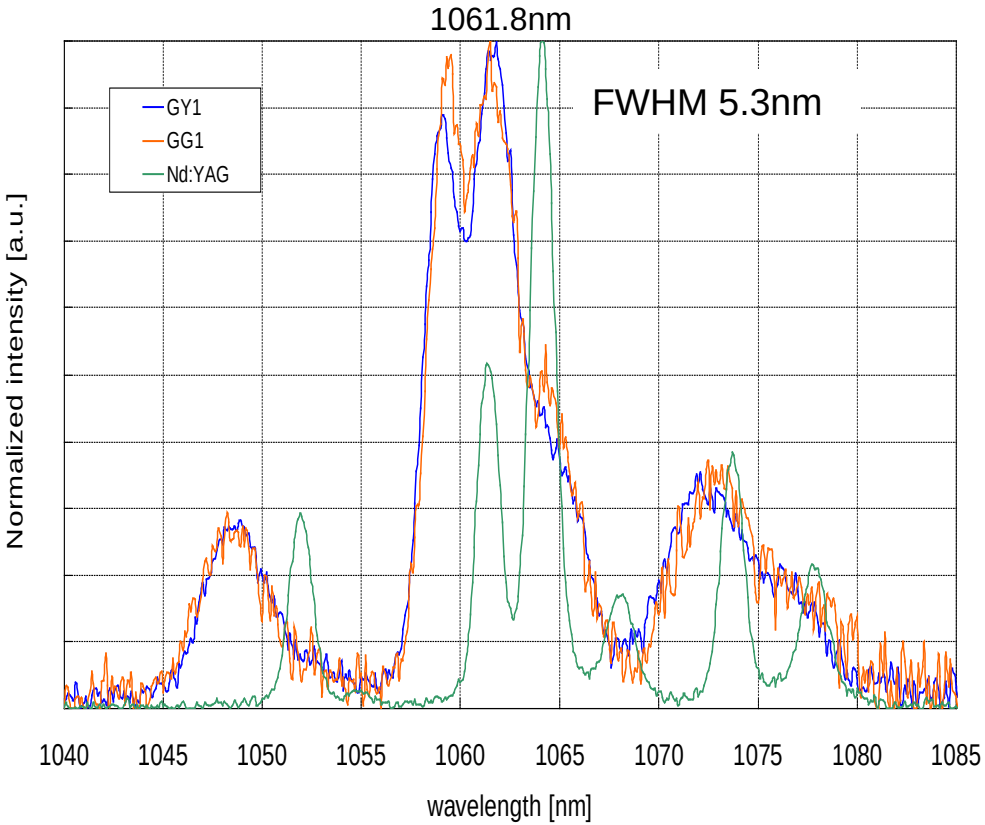
Absorption & Emission spectra of Nd mixed garnet ceramics

Absorption



Absorption peak wavelength is almost the same as that of Nd:YAG, but the absorption coefficient is smaller than that of Nd:YAG

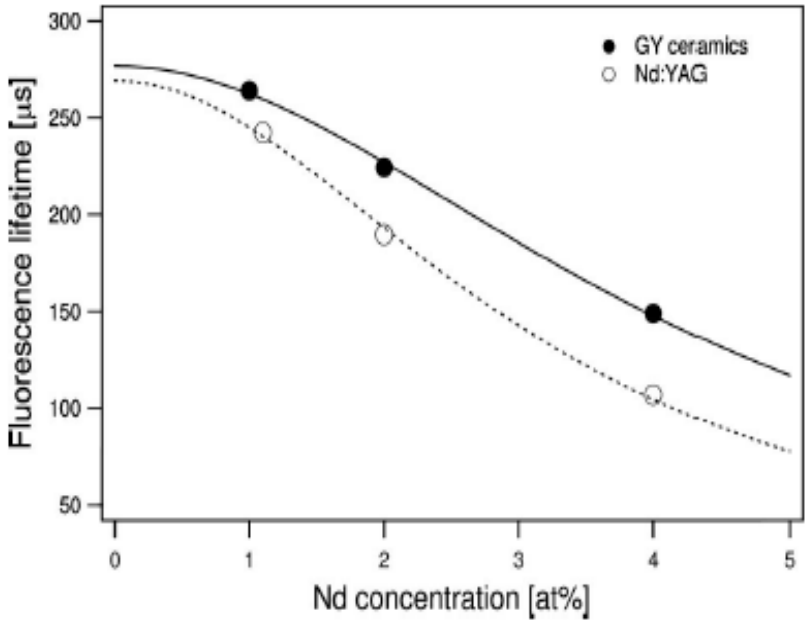
Emission



The emission bandwidth is about 3 times broader than that of Nd:YAG

H.Okada et al, Optics letters, vol35,No18, (2010)3048

physical properties



Lifetime

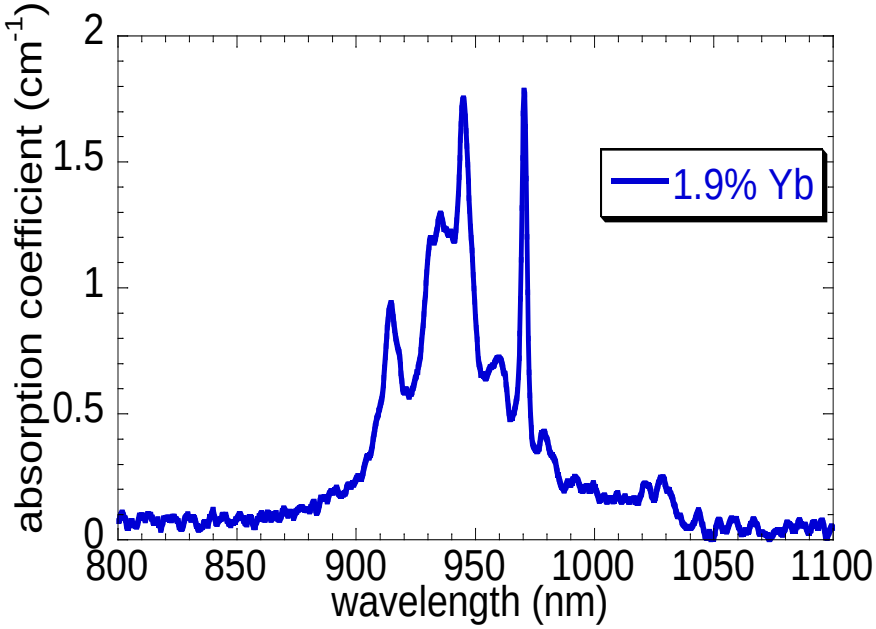
Nd	mixed garnet	YAG
1%	264 μs	242 μs
2%	224 μs	190 μs
4%	149 μs	107 μs

Lifetime is longer than that of Nd:YAG

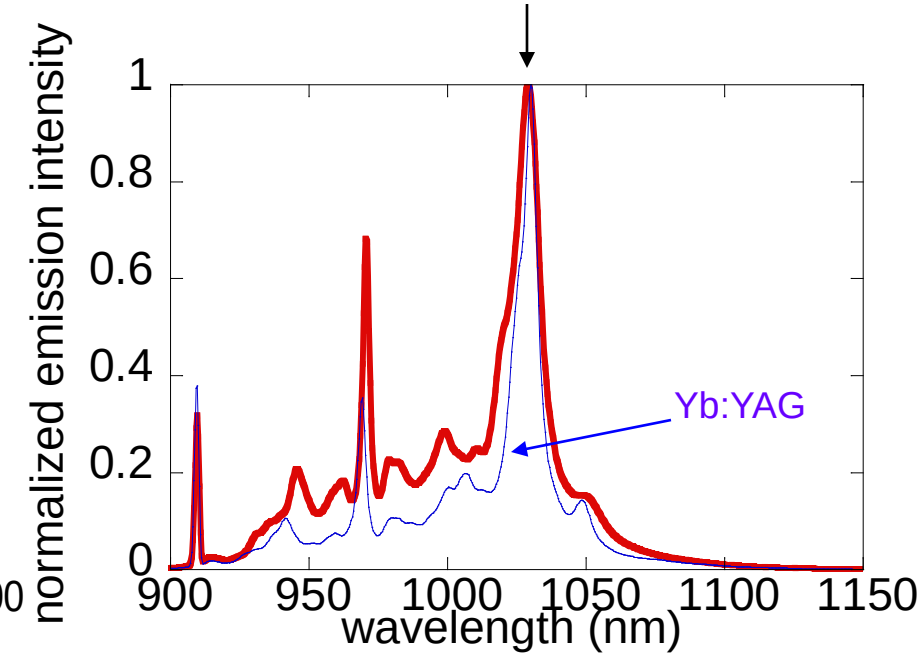
Emission cross section ($^4F_{3/2}$-$^4I_{11/2}$)	7.8×10^{-20}cm^2
Refractive index	~ 1.9 (@633nm)
Thermal conductivity	5.1 W/mK

Absorption & Emission spectrum of 1.9%Yb:$(Y_1Gd_2)Sc(Ga_1Al_2)O_{12}$ ceramics

1.9%Yb: $(Y_1Gd_2)Sc(Ga_1Al_2)O_{12}$
Thickness:1.15mm



Peak ~ 1029.5nm



Absorption spectrum

FWHM @ 945 nm = ~22 nm

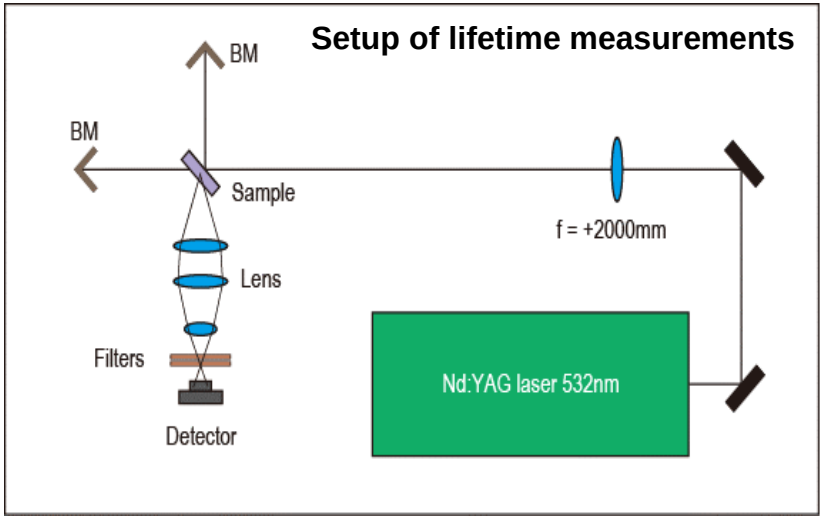
@ 970 nm = ~3 nm

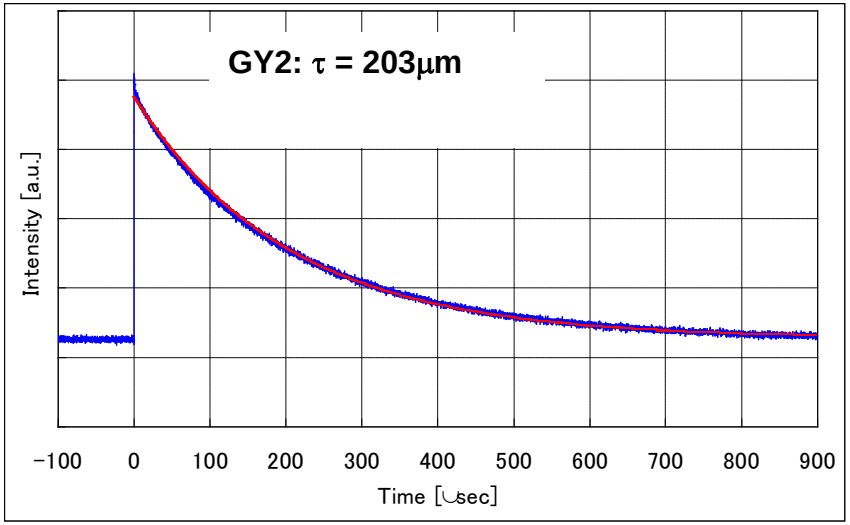
Emission spectrum

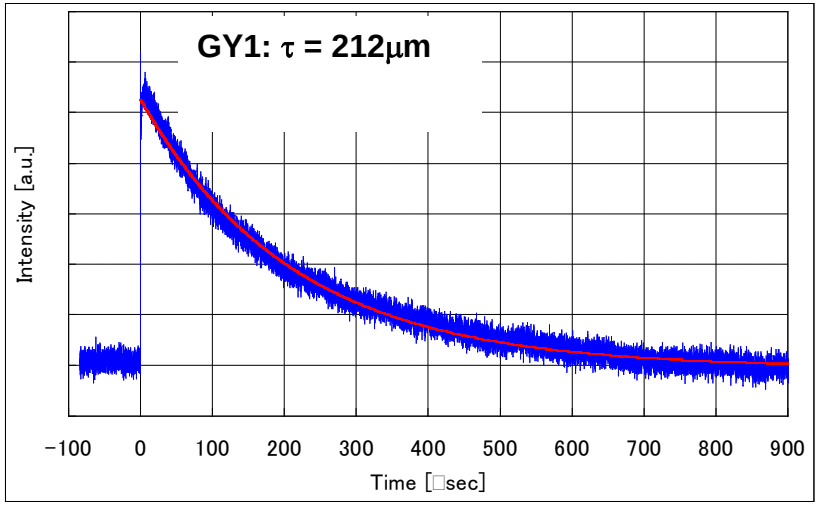
FWHM: ~ 14 nm

(YAG: ~ 9 nm)

Lifetime of disordered ceramics





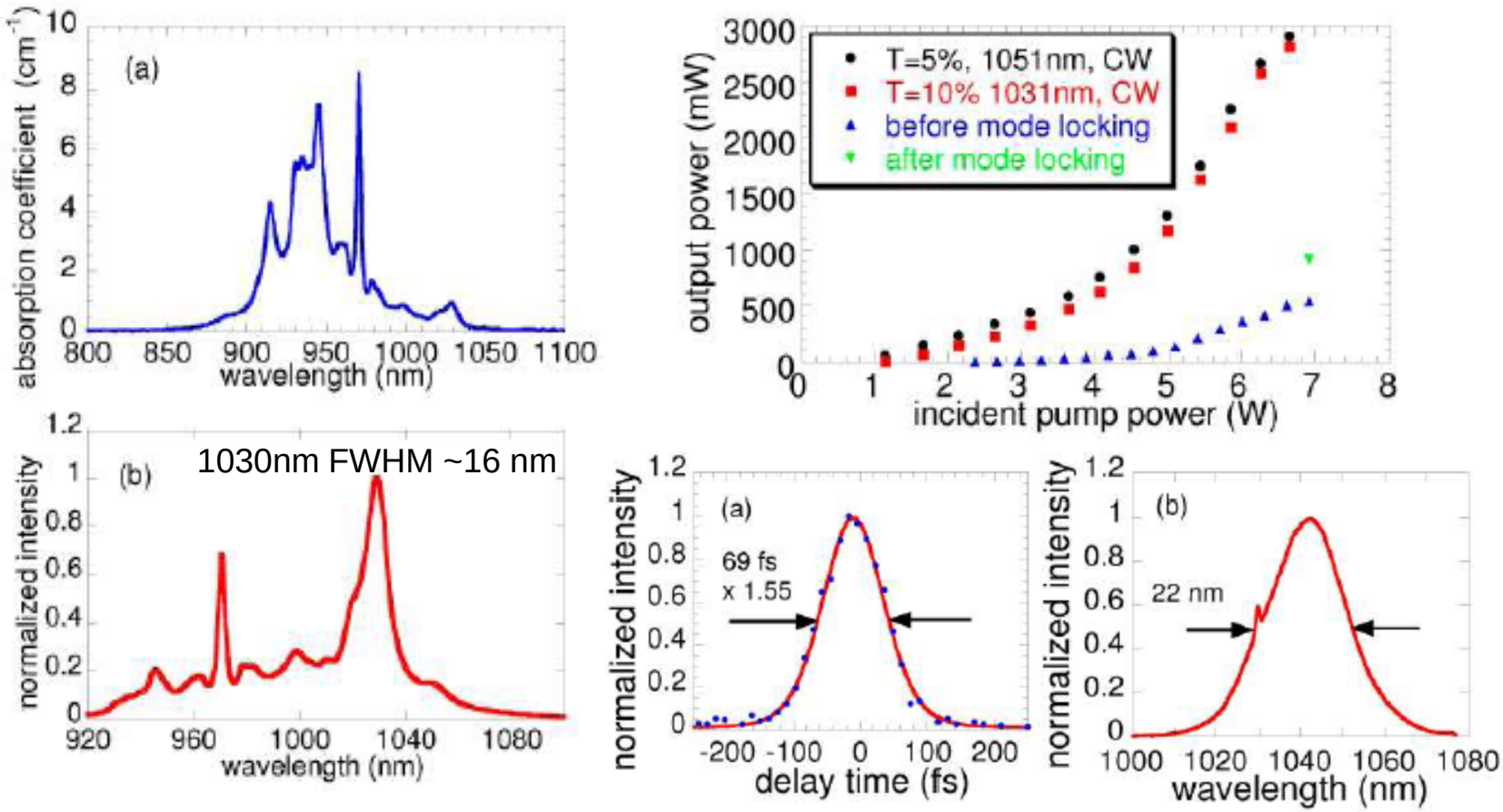


Sample	Nd (%)	lifetime (μsec)
GY1	1.0	213
GY2	2.0	203
GY4	4.0	123
GG1	1.0	235

This research was partially supported by “C-PhoST: Consortium for Photon Science and Technology” program funded by the Ministry of Education, Culture, Sports, Science and Technology (MEXT) of Japan.

10%Yb:$(YGd_2)Sc_2(Al_2Ga)O_{12}$ ceramic laser

Yb-doped mixed garnet ceramic laser was demonstrated by Dr.Tokurakawa.In mode-locked laser operation, pulse as short as 69 fs with the average power of 0.8W was achieved.

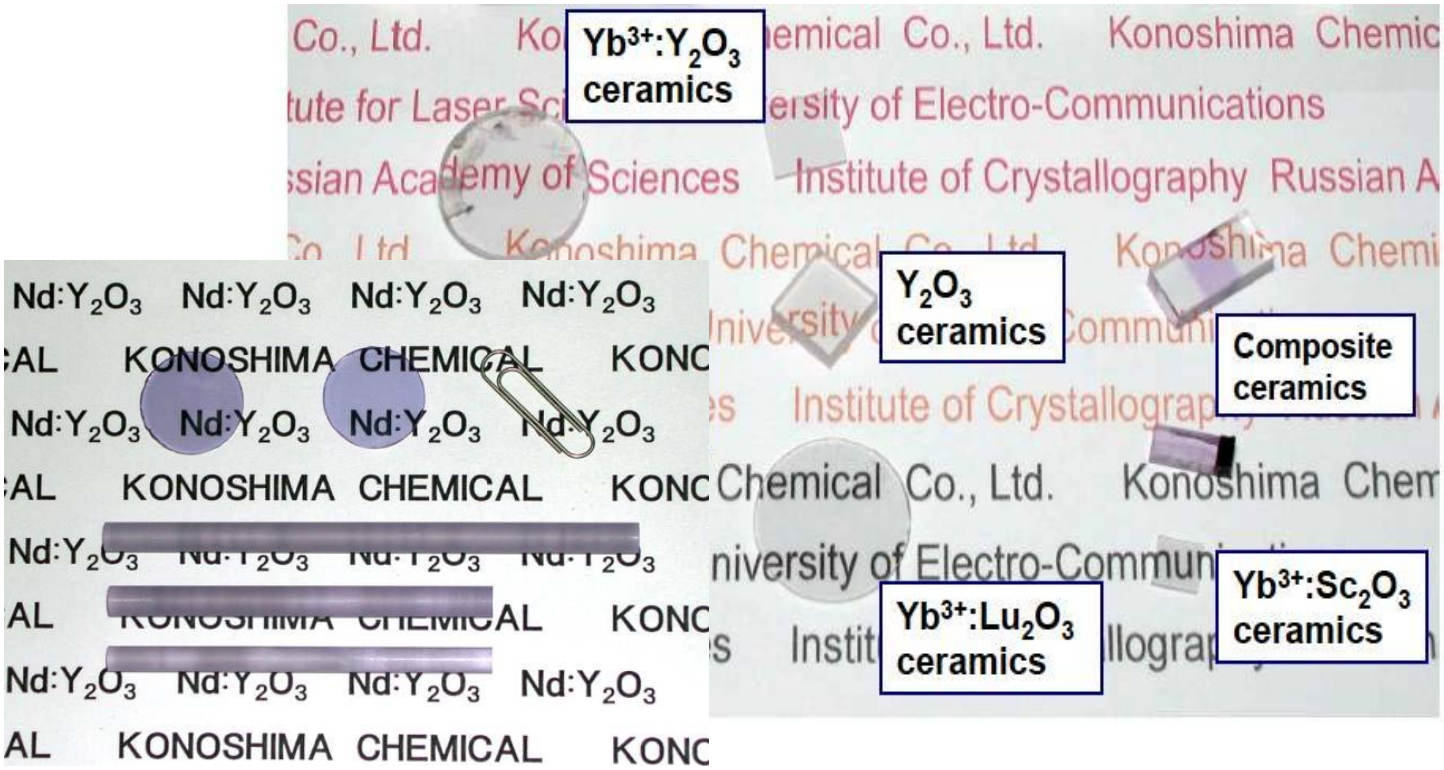


M.Tokurakawa, Optics Express, 18 (2010) 4390

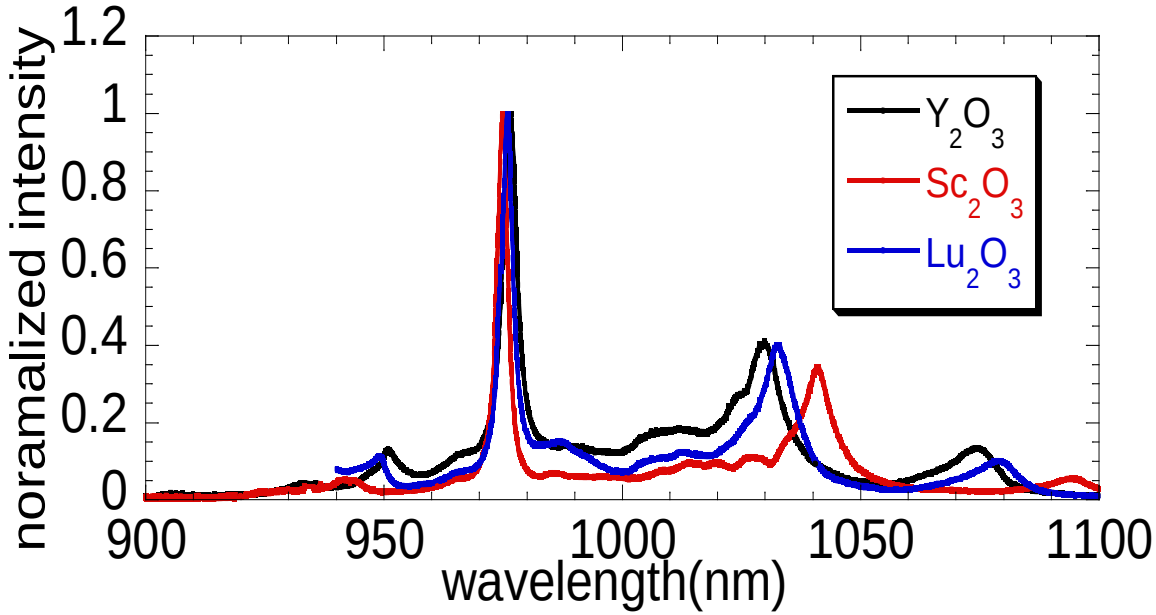
Mixed garnet ceramics material is attractive for mode-looked laser operations

Sesquioxide ceramics

Feature: Highly thermal conductivity, Broad spectrum



Emission spectra of $Yb^{3+}:Re_2O_3$



	Emission peak (nm)	FWHM (nm)	Transform limit (fs)	Emission peak (nm)	FWHM (nm)	Transform limit (fs)
$Yb^{3+}:Y_2O_3$	1031	15	74	1075	16	76
$Yb^{3+}:Lu_2O_3$	1032	13	86	1080	15	82
$Yb^{3+}:Sc_2O_3$	1041	11.5	99	1094	17	74
$Yb^{3+}:Y_3Al_5O_{12}$	1030	8	139			

he emission spectra of Yb:sesquioxide are about 1.5~2 times broader than that of Yb:YAG

Comparison of thermal conductivity

Sesquioxide

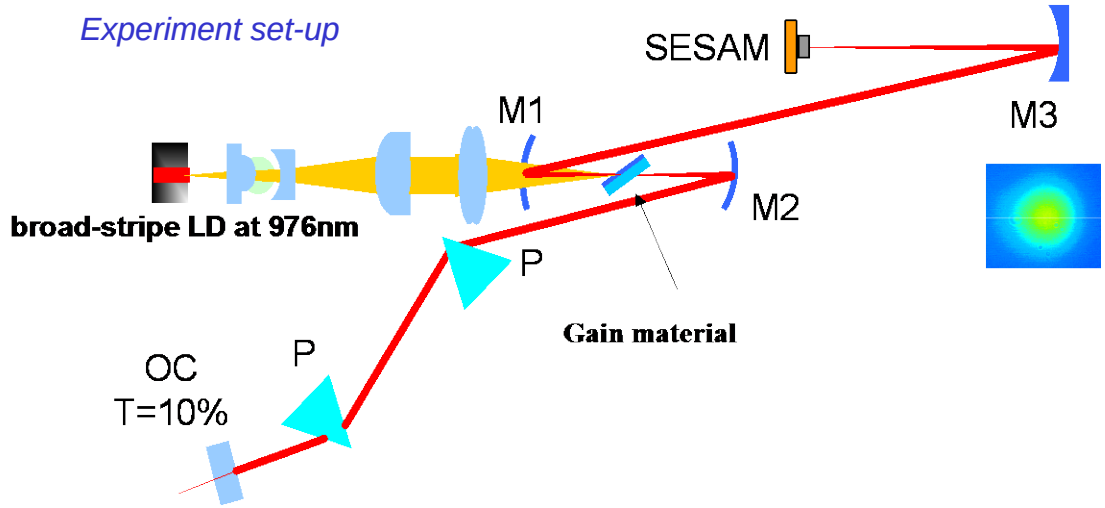
materials	KYW	YVO_4	YAG	Y_2O_3	Lu_2O_3	Sc_2O_3
Melting point(C°)			1930	2430	2450	2430
Thermal conductivity non-doped W/mK	3.8	5.23 12.1	11 10.1	13.6	12.5	16.5
Thermal conductivity ≈ 3%Yb W/mK			6.8 (5%)	7.7	11.0	6.6
references	F. Druon *et al.* Opt. Express **12**, 5005(2004)	V.E.Kisel *et al.* Opt. Lett **30**, 1150 (2005) Y. Sato *et al.* Opt. Express **14**, 10528 (2006)	U. Griebner *et al.* Opt. Express **12**, 3125 (2004) Y. Sato *et al.* Opt. Express **14**, 10528 (2006)	U. Griebner *et al.* Opt. Express **12**, 3125 (2004)	U. Griebner *et al.* Opt. Express **12**, 3125 (2004)	U. Griebner *et al.* Opt. Express **12**, 3125 (2004)

High thermal conductivity → advantage for a high power laser

Kerr-lens mode-locked Yb:ceramic laser

The highest power operation for a sub 100 fs Yb doped DPSSL was carried out with ceramic material

Experiment set-up



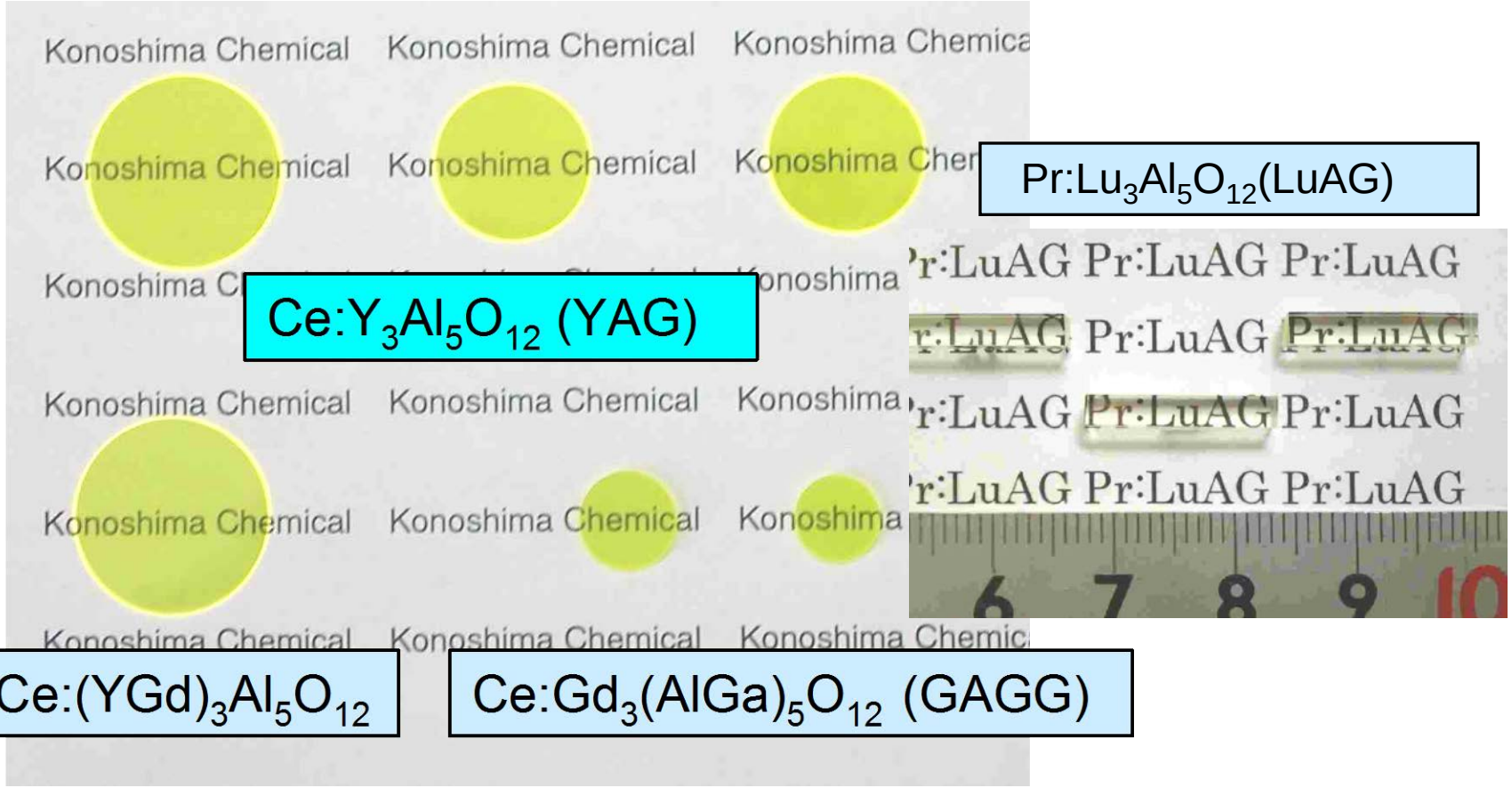
Results

Gain material	P_{max} (mW)	Δ t (fs)	Efficiency (%)	Pump source	Ref.
$Yb^{3+}:Sc_2O_3$ with $Yb^{3+}:Y_2O_3$	1500 1000	66 53	18.8 12.5	8 W LD	
$Yb^{3+}:Sc_2O_3$	850	92	19	4.5 W LD	M.Tokurakawa *et al.* Opt. Lett, 32, 3382
$Yb^{3+}:Lu_2O_3$ with Y_2O_3	320	65	7.1	5W FCLD	M.Tokurakawa *et al.* accepted to Opt. Lett,

Sub-100fs Yb-doped solid-state lasers were already achieved by directly LD pumping

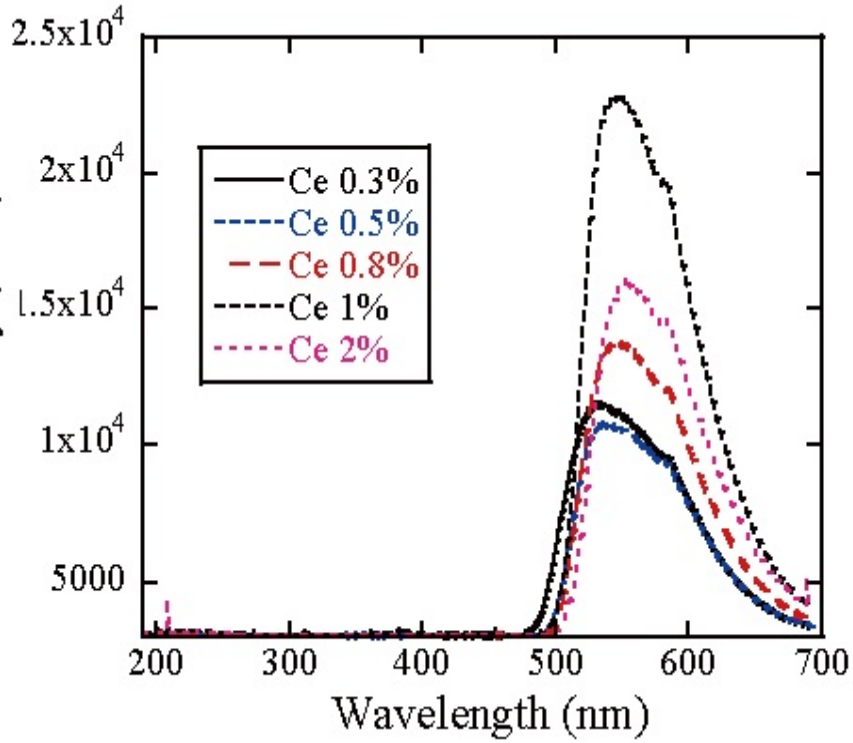
Scintillator ceramics

Scintillator and phosphor are important application for the transparent ceramics.

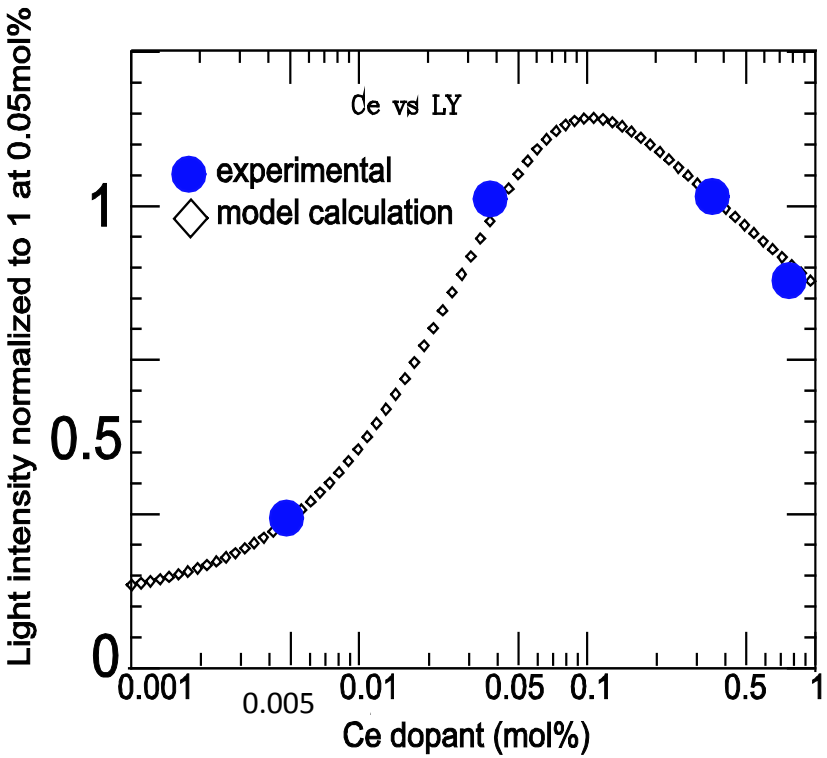


Ce:YAG scintillator

X-ray induced radioluminescence



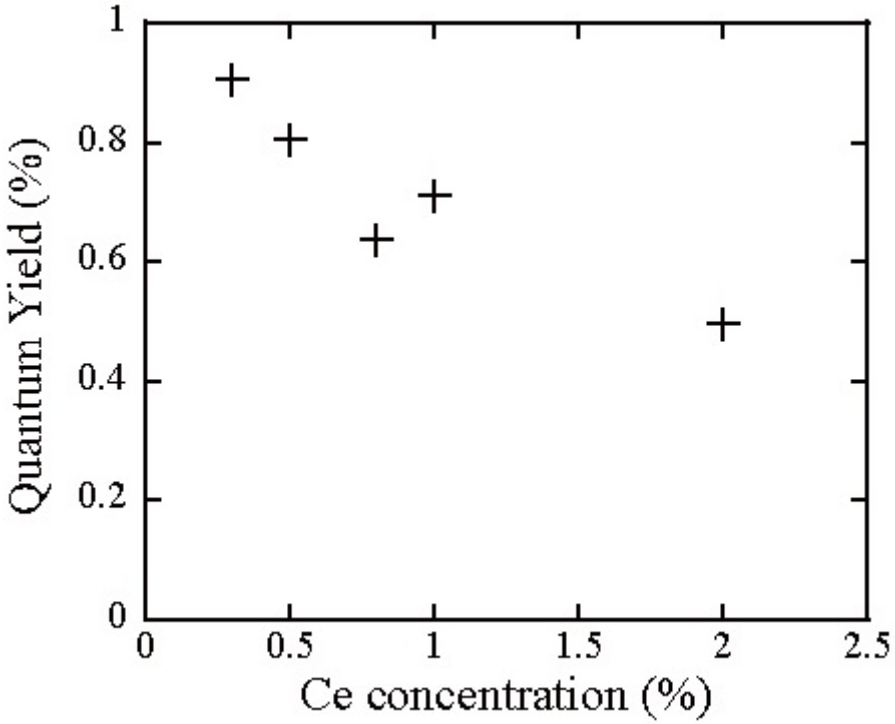
γ-ray induced light yield



T. Yanagida et al. , IEEE. Nucl. Trans. Sci., 51 1836 (2005).

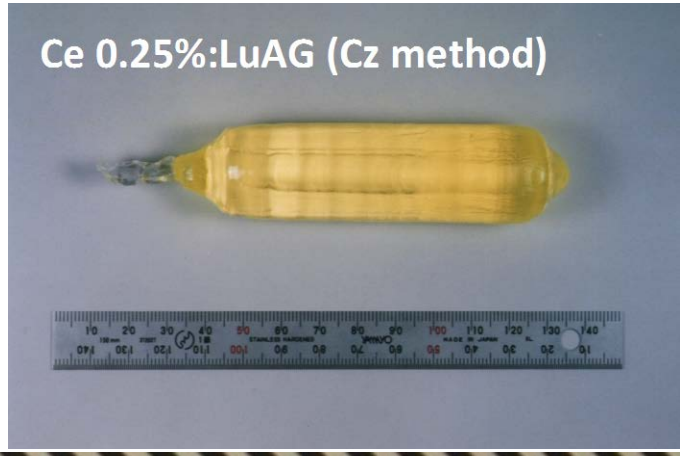
Ce:YAG scintillator ceramics

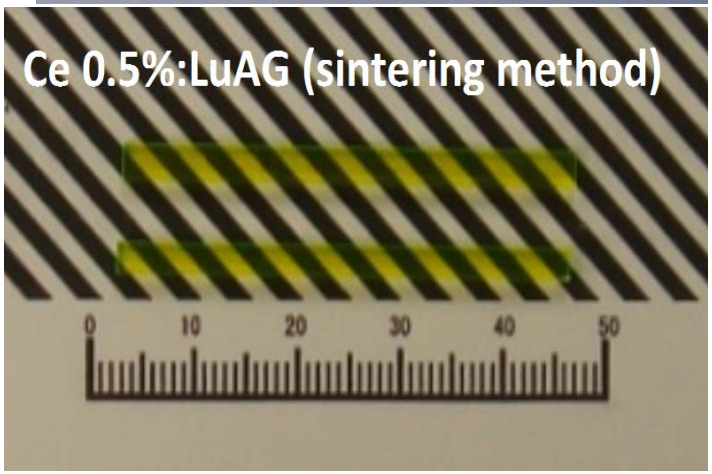
PL absolute Quantum yield ofYAG:Ce

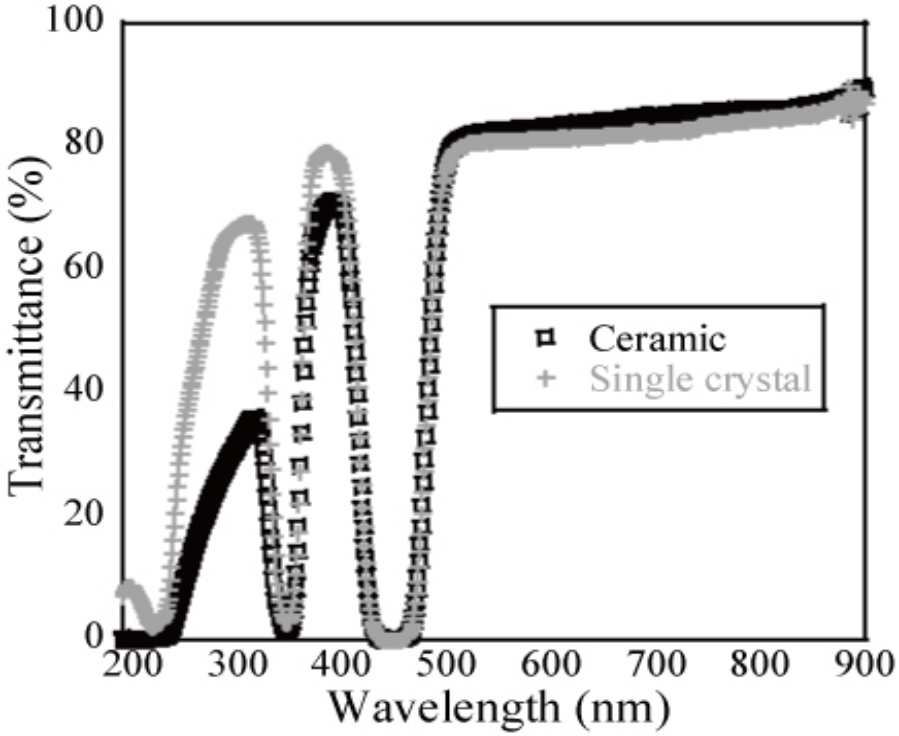


Ce:LuAG ($Lu_3Al_5O_{12}$) scintillator ceramics

It is difficult to grown highly doped Ce (>0.25%):LuAG by Cz method (also Pr). 0.5%Ce:LuAG ceramics were successfully fabricated.





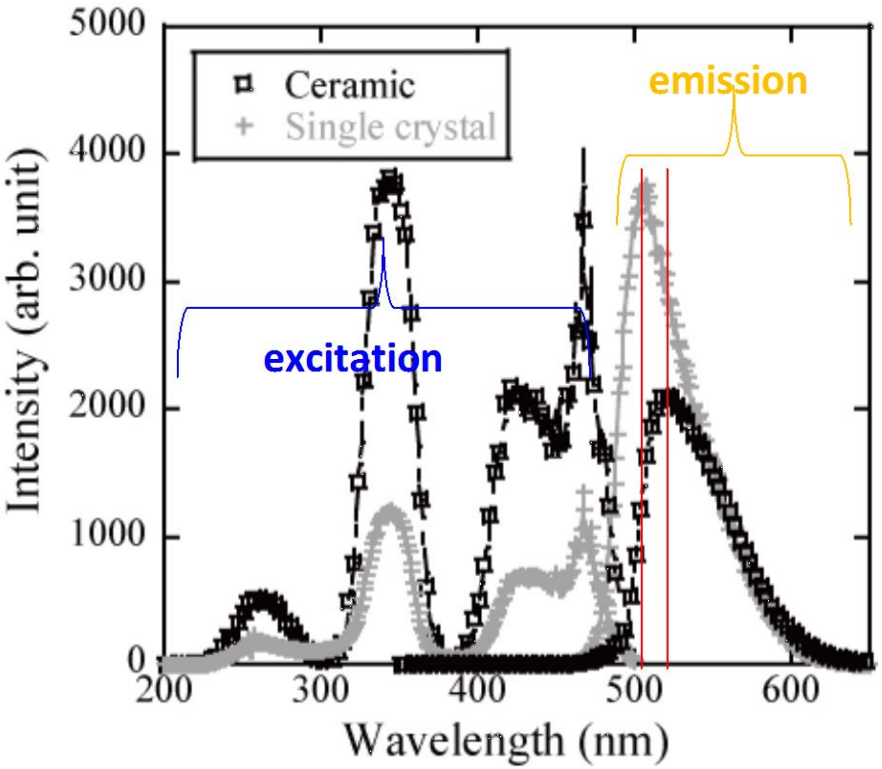


Transmittance ~ 80% at wavelength longer than 500 nm for both samples. Absorption lines appear at 230, 340, and 460 nm due to Ce^{3+} 4f-5d transition. The ceramic shows higher absorption than single crystal.

Ce:LuAG scintillator ceramics

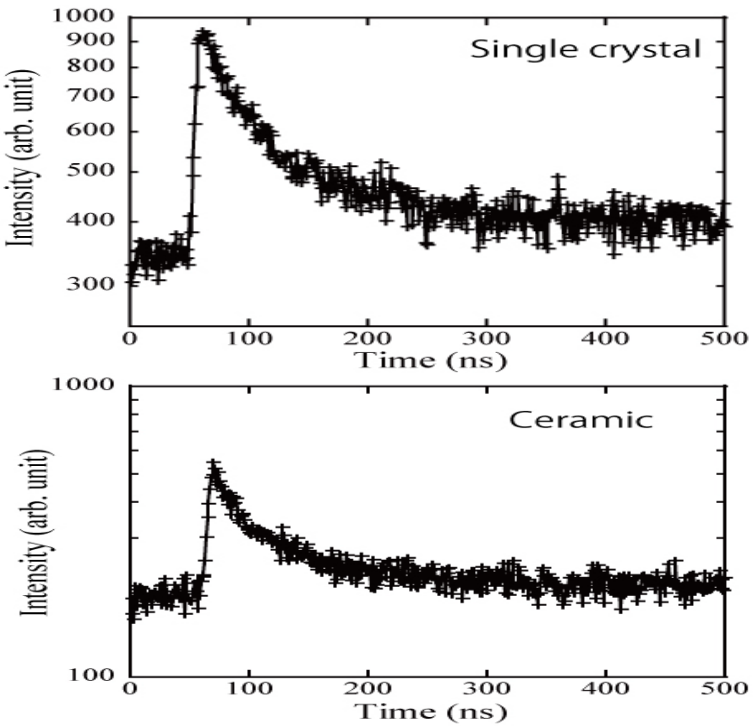
Photoluminescence

Excitation wavelength = 345 nm



Emission peaks of the single crystal and the ceramic were ~500 and ~520 nm. The emission peak of the ceramic slightly shifts to longer wavelength.
Si-APD is suitable to readout scintillation photons.

20-30 keV X-ray excited decay time profiles



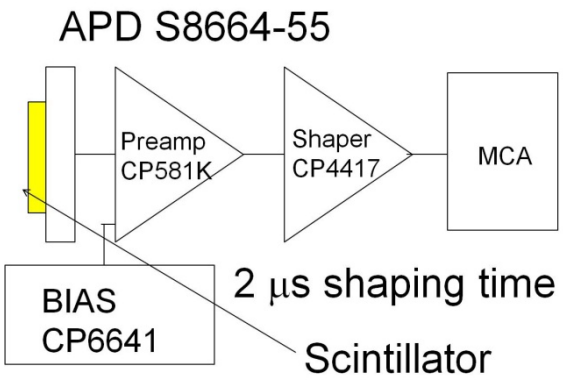
	Main component (ns)	Secondary component (ns)
Ceramic	37.3 ± 2.6	300 ± 60
Single	46.1 ± 2.0	576 ± 97

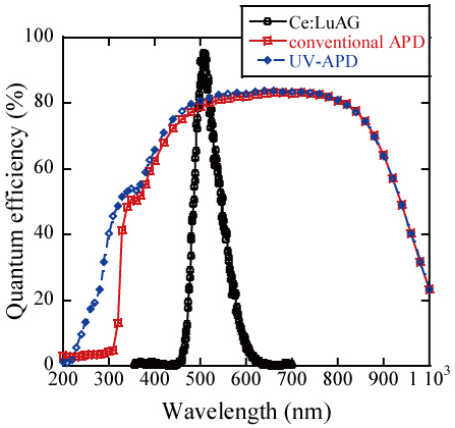
Ceramic shows faster decay owing to higher Ce concentration

Measured by Dr. T.Yanagida, IMRAM Tohoku University Japan

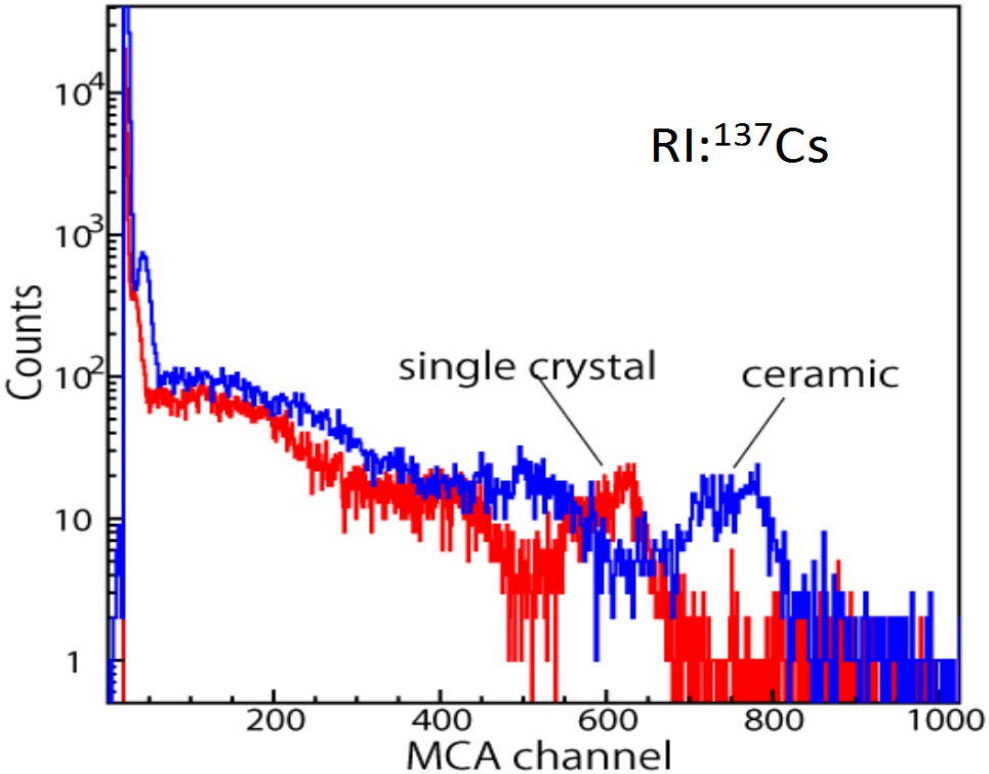
Ce:LuAG scintillator ceramics : Light yield

Experimental setup





Energy spectra of Ce:LuAG



MCA channel is calibrated by using ^{55}Fe 5.9 keV peak (=1640 e-h)
The light yields of the single crystal and the ceramic are ~12000 ph/MeV and ~16000 ph/MeV

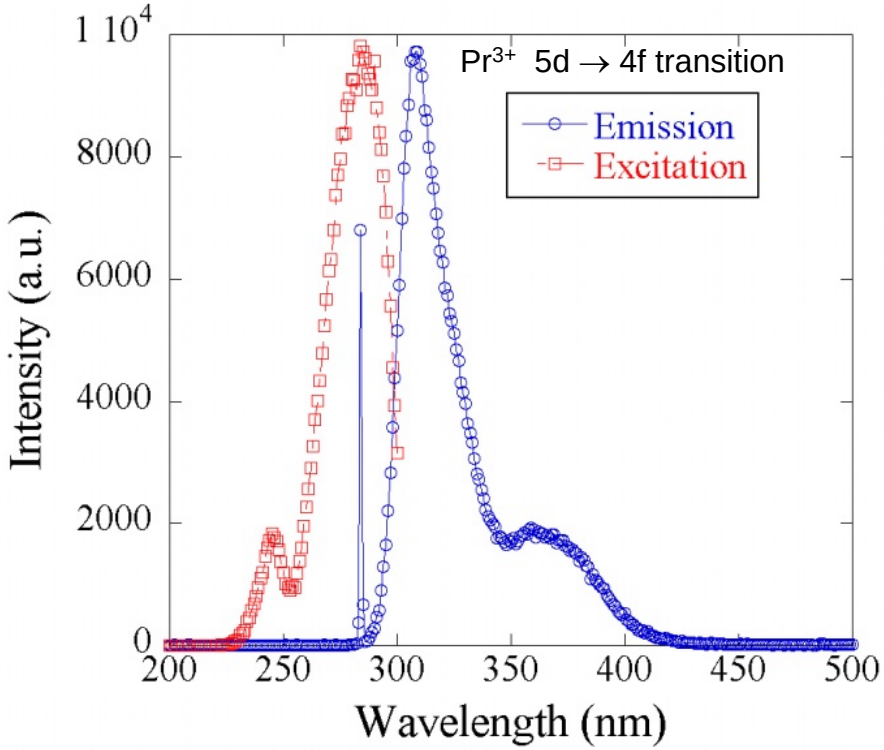
Light yield of ceramics was 30% larger than that of the single crystal

Measured by Dr. T.Yanagida, IMRAM Tohoku University Japan

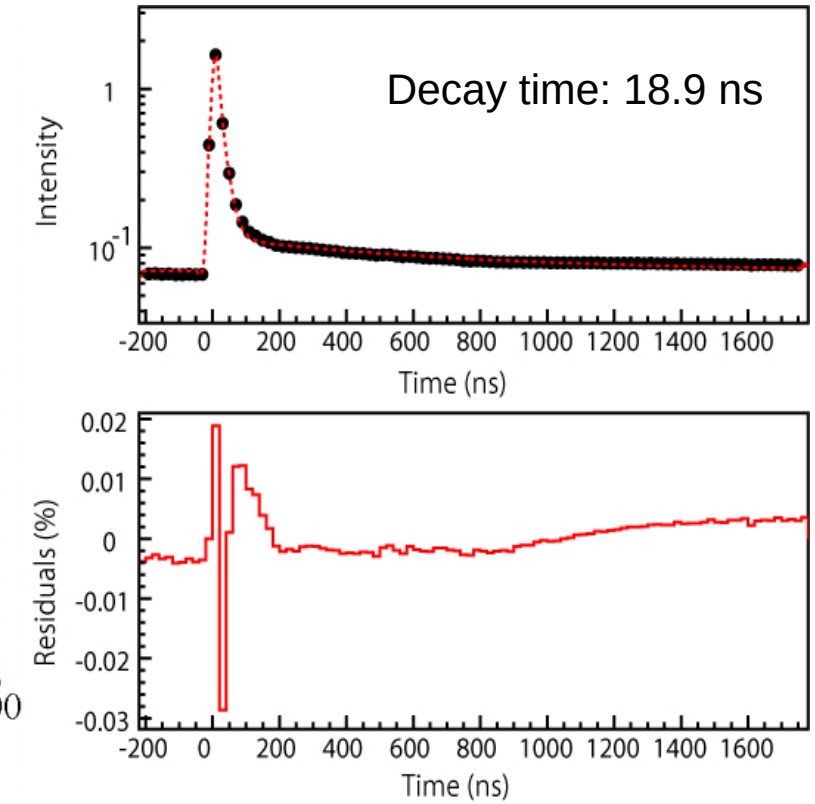
0.25%Pr:LuAG ceramics

Emission & Excitation spectra

Peak emission: 310 nm



Decay profile excited by ^{137}Cs



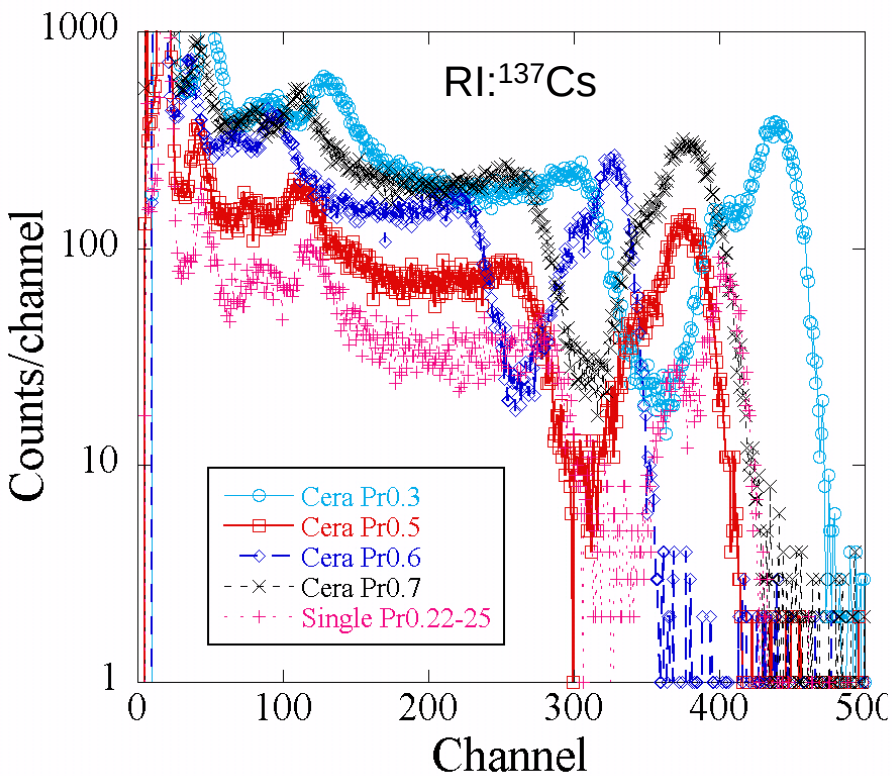
Emission peak wavelength and decay time of Pr:LuAG ceramics is almost the same as those of single crystal

Measured by Dr. T.Yanagida, IMRAM Tohoku University Japan

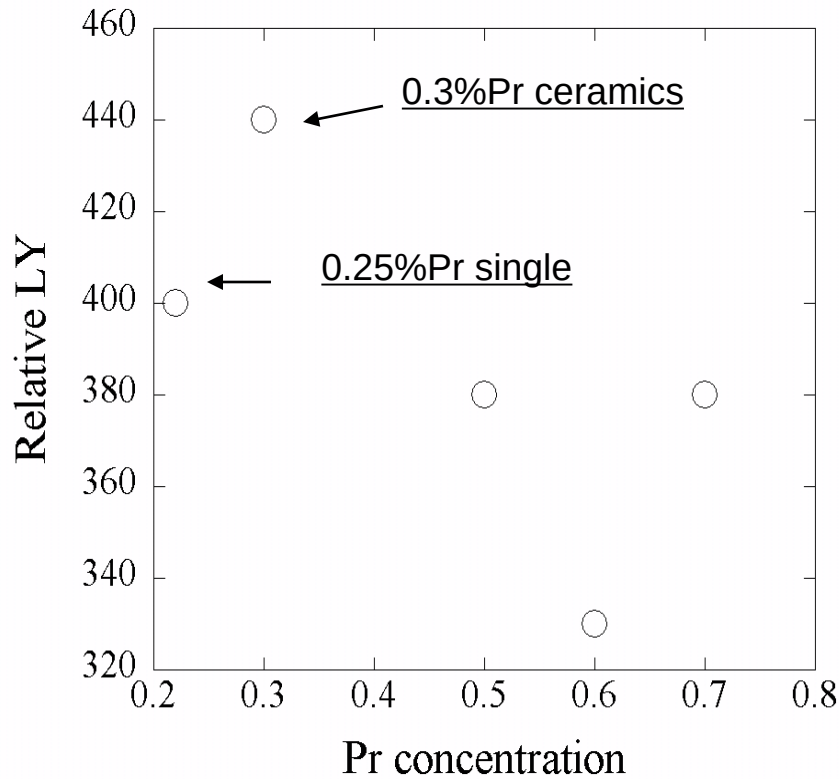
Pr:LuAG ceramics

Light yield of 0.25%Pr:LuAG single crystal and Pr(0.3,0.5~0.7%):LuAG ceramics were measured .

energy spectra



Pr concentration v.s. relative light yield

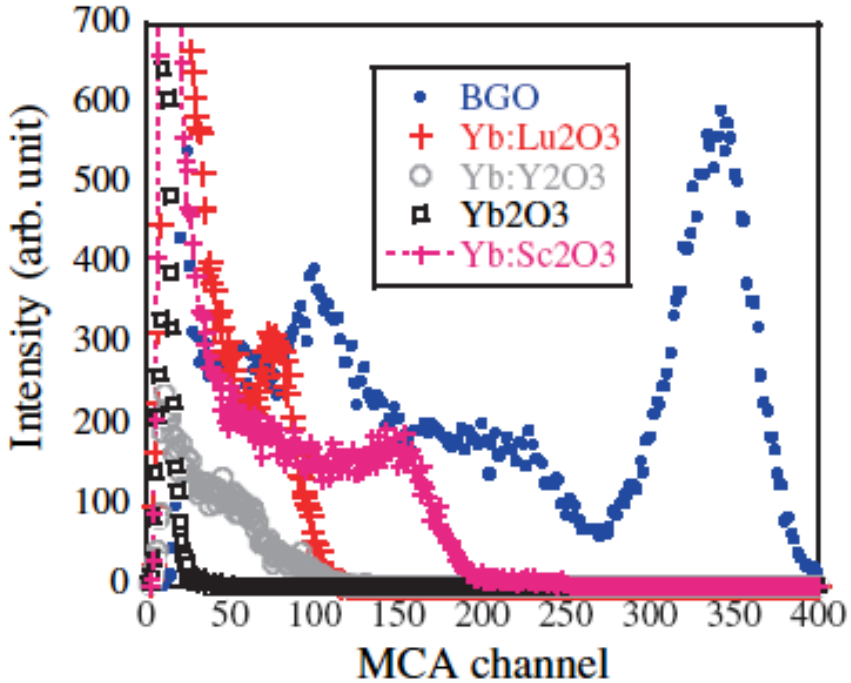


Light yield of 0.3%Pr:LuAG ceramics was 10% larger than that of the single crystal

Measured by Dr. T.Yanagida, IMRAM Tohoku University Japan

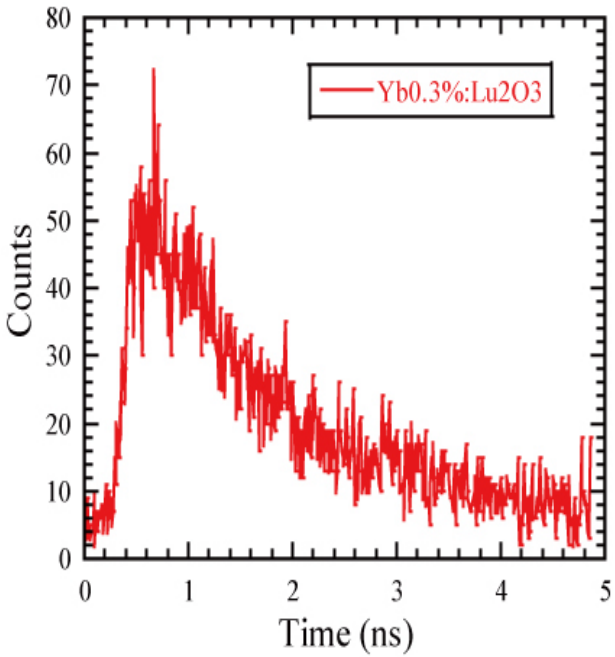
Yb-sesqui-oxide ceramicscintilltor

Energy spectrum



. ^{137}Cs pulse height spectra of conventional BGO (blue), Yb:Lu_2O_3 Yb:Y_2O_3 (green), Yb_2O_3 (black), and Yb:Sc_2O_3 (cyan). The vertical scaled for comparison.

decay profile



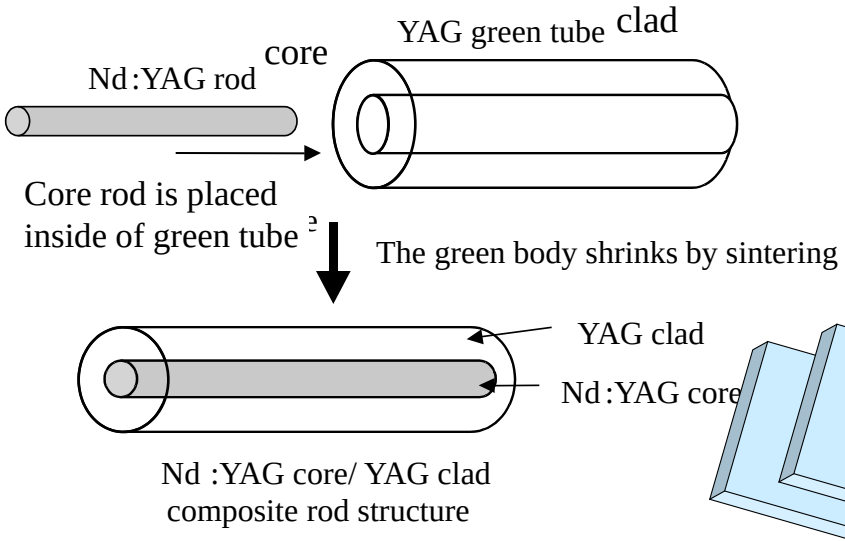
Ulra farst decay time

Yb:Y_2O_3	0.12ns
Yb:Sc_2O_3	1.07ns
Yb:Lu_2O_3	1.93~2.0ns

T.Yanagida,Japan Appl. Phys Express(2011)126402

Fabrication of the composite ceramics

(I) Core/Clad structure

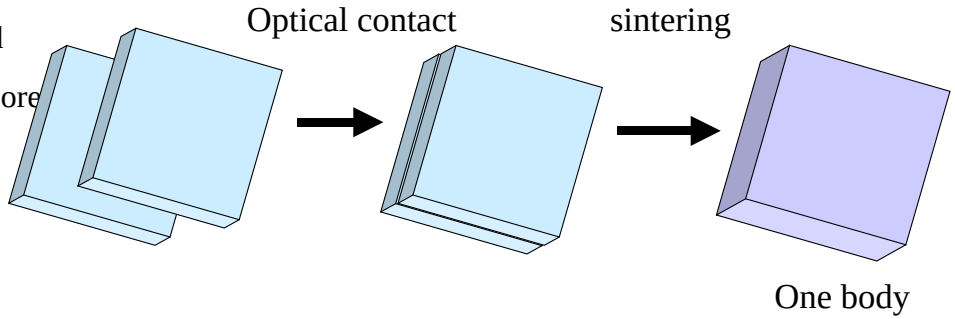


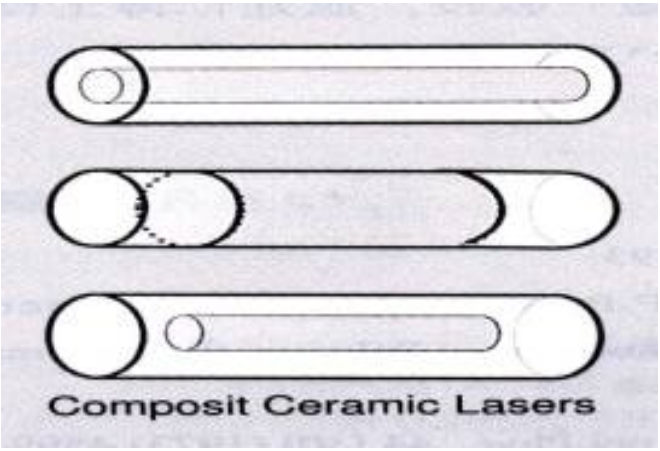
(II) Plate bonding

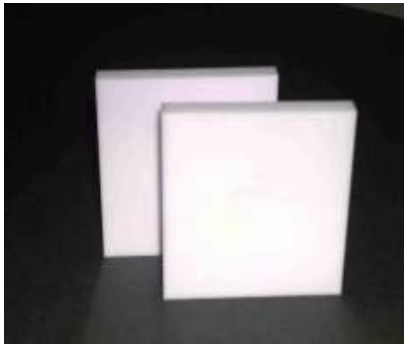
(1) Pre-sintered white ceramics are polished with precision (flatness < λ/10)

(2) Each ceramic bonds together by optical contact

(3)Final sintering





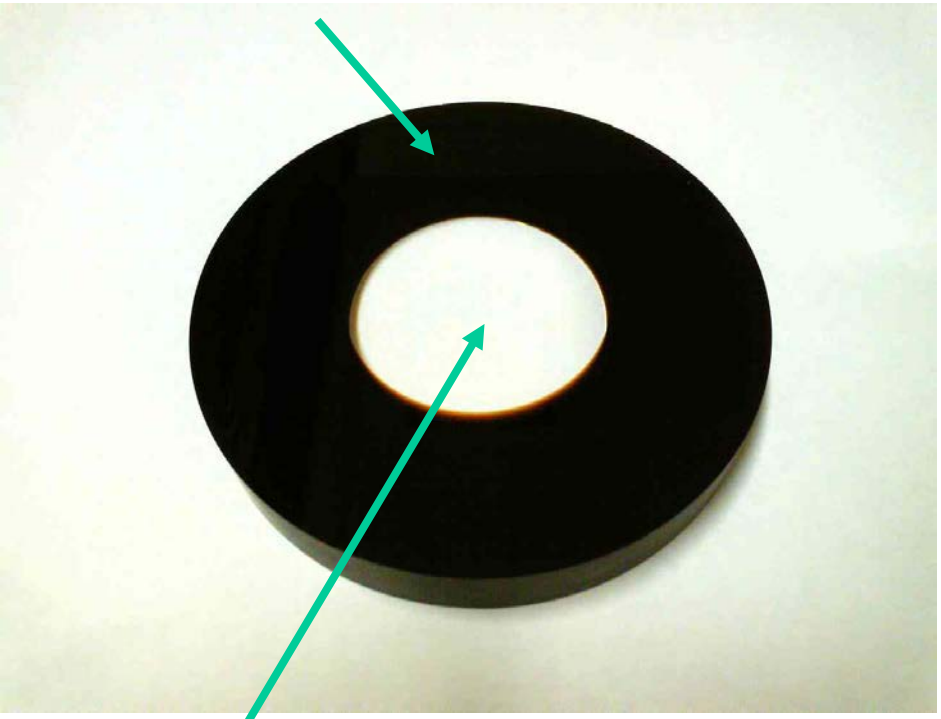


Cr^{4+}:YAG absorber for Yb:YAG laser

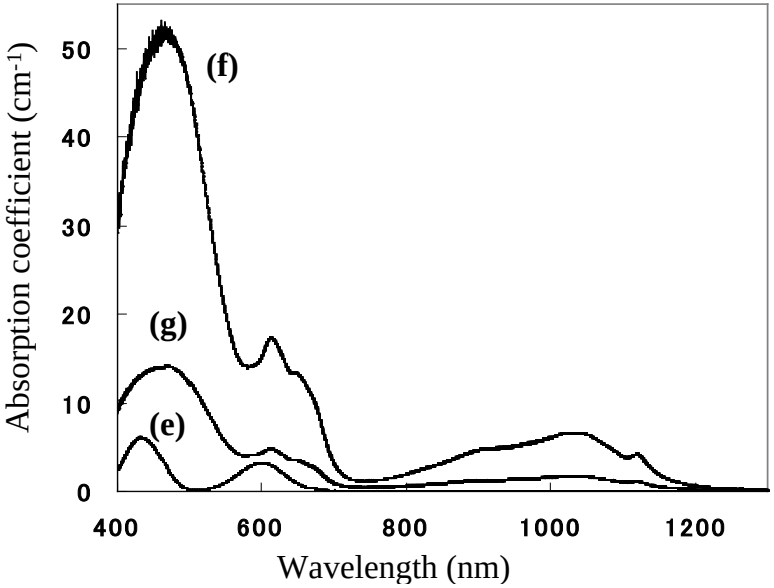
It Ytterbium doped laser material is attractive to the high power and high energy laser, because of lower quantum defect.

It is important to supression PO ASE for high-power laser, So gain material bonded absorber is suitable

Cr^{4+}:YAG



Yb:YAG



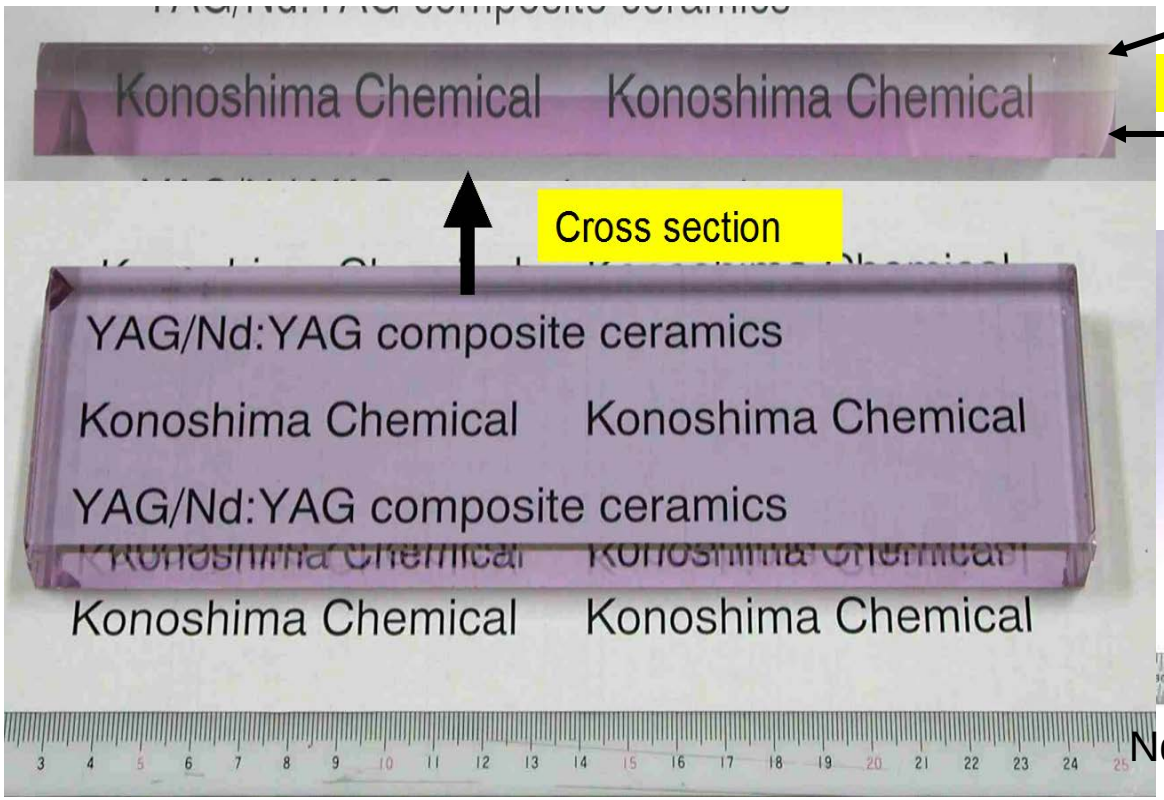
(e) as sintered,

(f) Cr^{4+}:YAG ceramics

(g) Cr^{4+}:YAG single crystal

Composite YAG laser ceramics

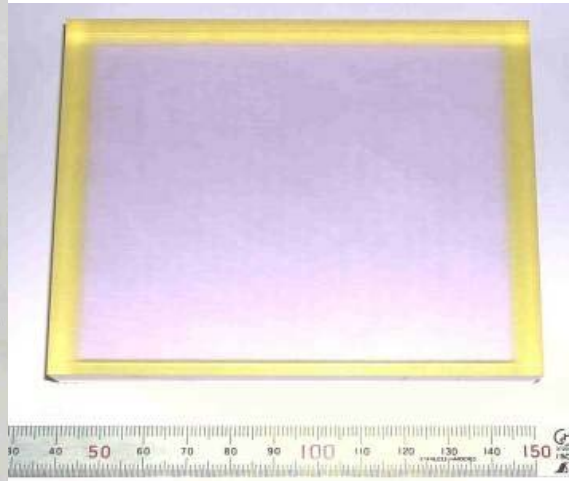
Recently, composite laser materials have been becoming the key parts for DPSSL. We are challenging to make large size composite ceramics with high optical quality.



YAG

No defect, scattering source

Nd:YAG



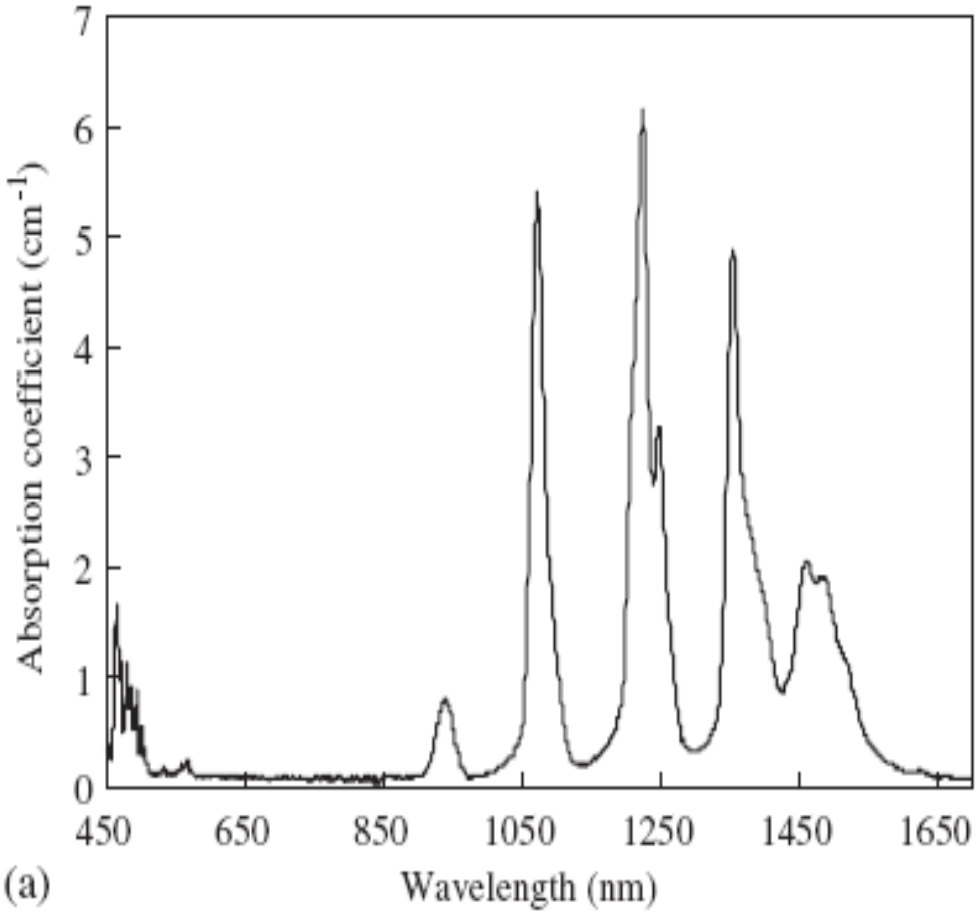
Nd:YAG/Sm:YAG composite slab for SSHCL

The latest Nd:YAG/YAG composite ceramic slab

length: ~ 20 cm

Sm^{3+}:YAG absorber for Nd:YAG laser

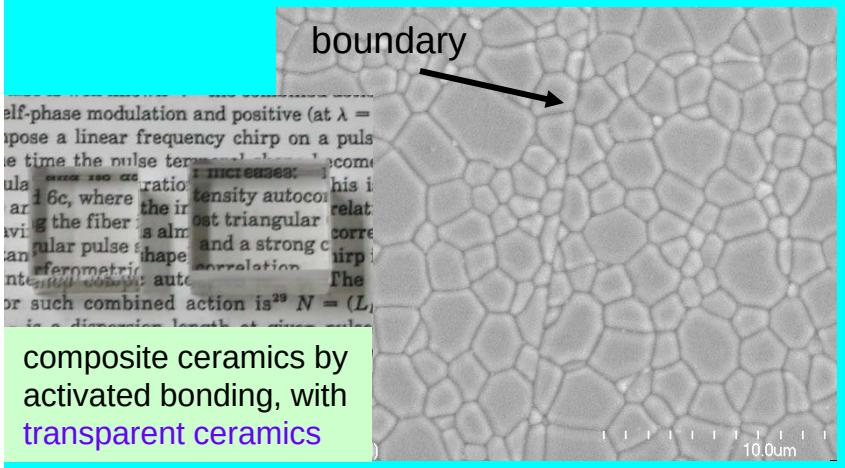
Absorption spectrum of Sm^{3+}:YAG



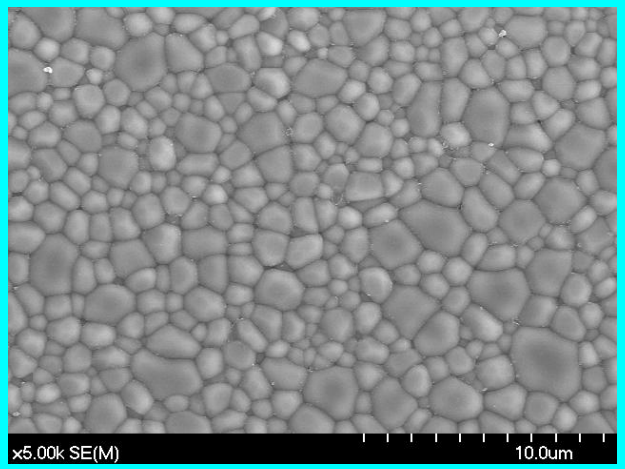
(a)

Typical bonging method vs. Ceramic bonding by sintering

Process	difficult (high precision polishing)	easy
	Low temperature (500-1300℃)	High(sintering) temperature (>1600℃)
	Need high-pressure ? (distortion?)	No pressure
Mechanism		
	O-H bonging, ion diffusion	Grain growth
Microstructure		



composite ceramics by activated bonding, with transparent ceramics



Strength	△（~80%of bulk strength)ref.	◎ (same as bulk strength)
Scattering(our results)	△	◎
Diffusion distance of dopant ions	short distance	long distance

Ref: Traggis, etc, : Proceeding of 11th Annual Directed Energy symposium, DEPS (2008)

Light Scattering at bonding boundary

As for test sample, we made three composite ceramics by sintering or activated bonding

Sample A: by sintering with pre-sintered ceramics

No scattering at the boundary

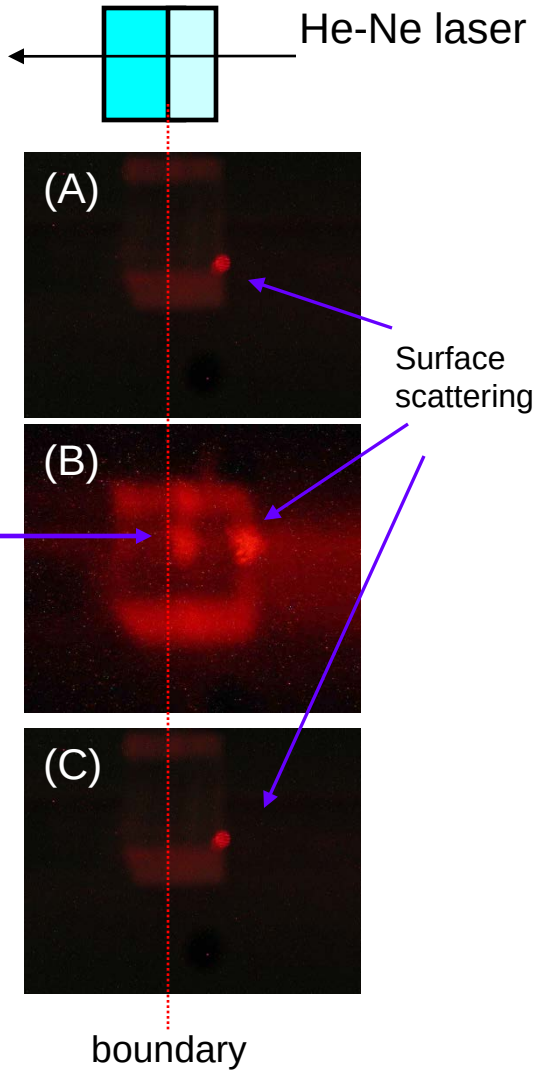
Sample B: by sintering with pre-sintered ceramics

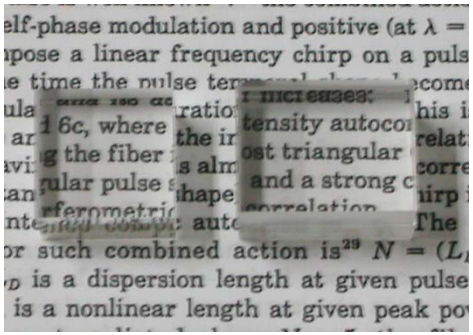
You can see the scattering at boundary with the naked eye or by using He-Ne laser

Sample C: by activated bonding with transparent ceramics

No scattering at the boundary

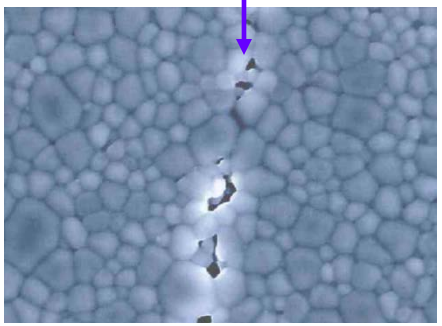
YAG/YAG composite ceramics





Sample C

boundary

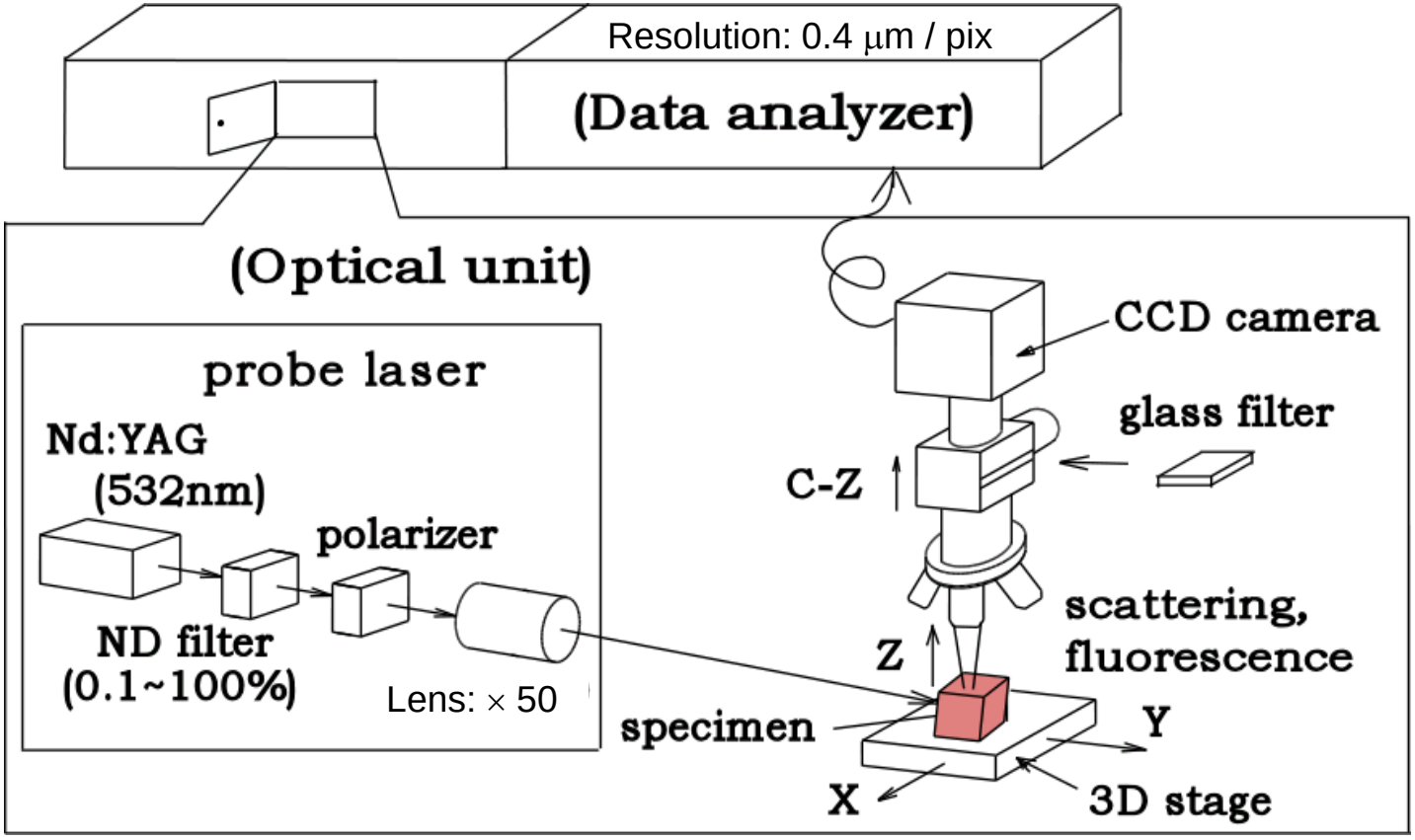


Microstructure of sample B (NG quality)

Laser tomography system for optical scattering measurements

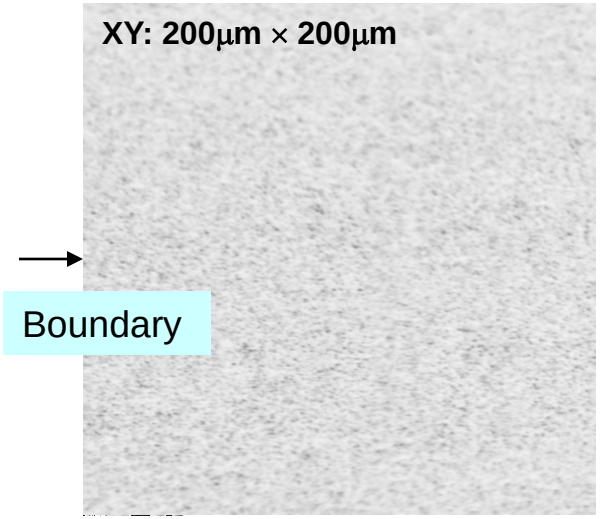
Laser tomography (Mitsui:MO-421): scattering signal form defects is detected by CCD camera

Prove laser: 2nd harmonic of CW Nd:YAG, beam spot size: φ10μm



Scattering of composite ceramics

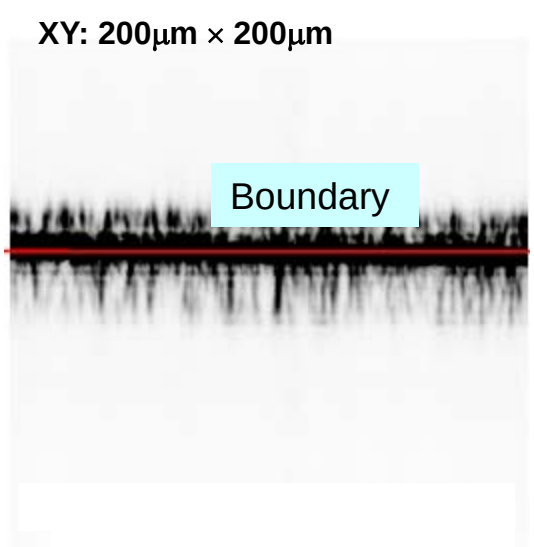
Sample A (by sintering)



Prove intensity: 90mW

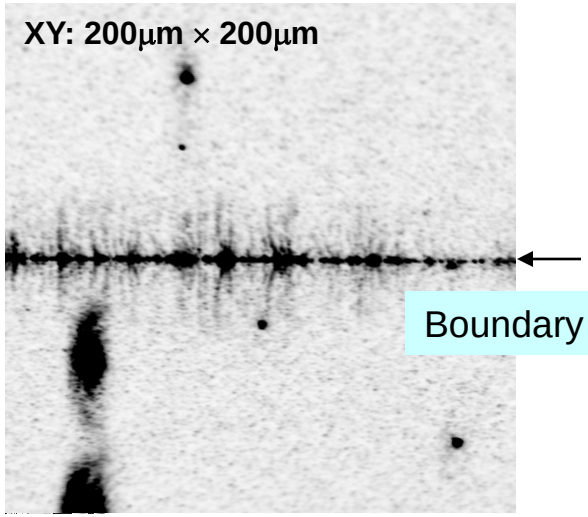
Light scattering intensity: 6

Sample B (No good)



Prove intensity: 0.9mW

Sample C (by activated bonding)



Prove intensity: 0.9mW

Light scattering intensity: 100

Scattering density: ~1.5×10^{10} /cm^3

(Same as that of bulk)

Sample A (composite by sintering) has no light scattering at boundary region

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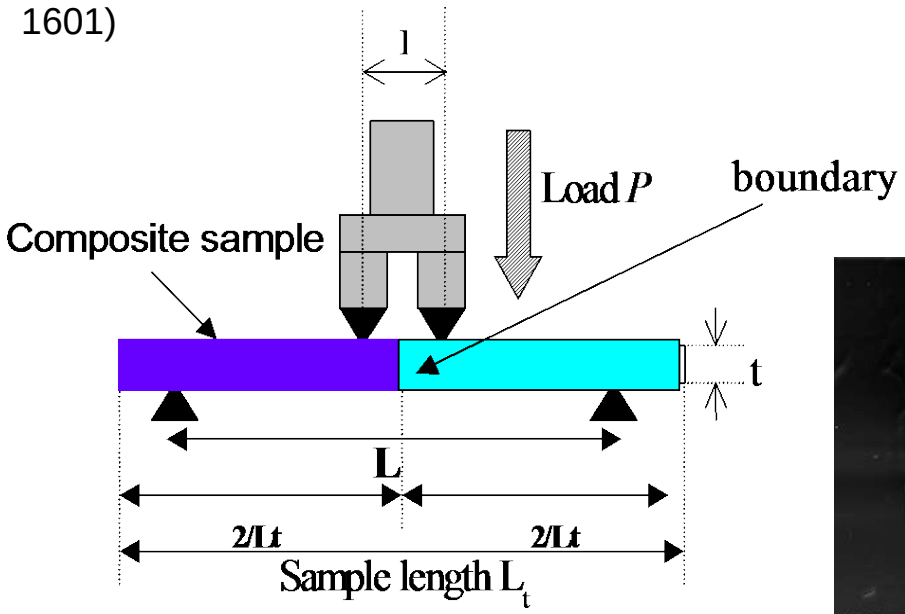
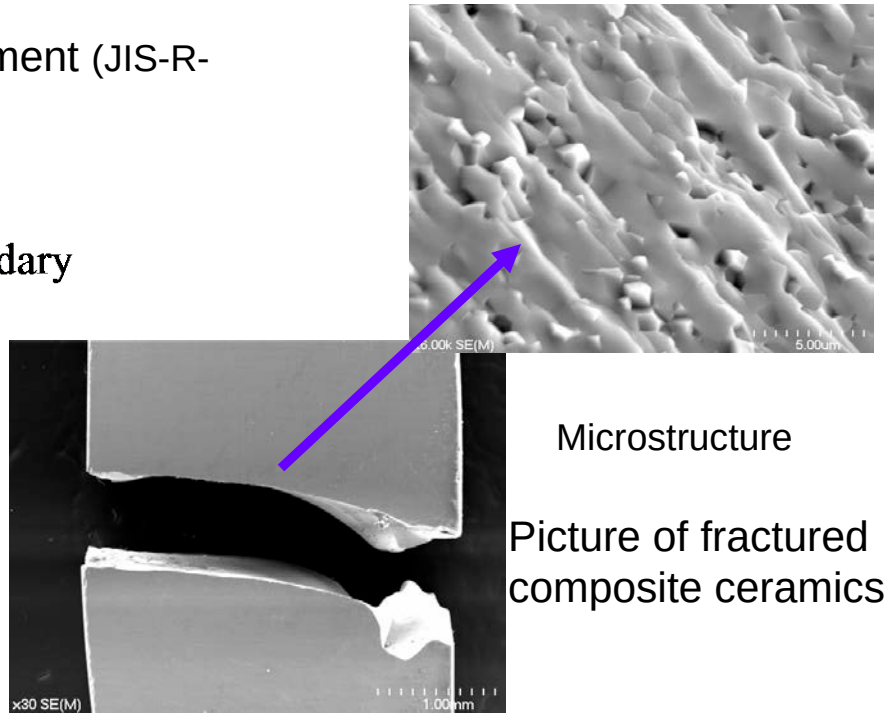
Bonding strength (Four-point fracture strength measurement)

The diagram of fracture strength measurement (JIS-R-1601)





Microstructure

Picture of fractured composite ceramics

Fracture strength: 3P(L-1) / 2wt^2

Bonded ceramics by sintering: 341.7 ± 58.3MPa

Ceramics : 360.8± 49.2MPa

The strength of composite by sintering and ceramics is the same within a error

(Ref.) Strength by activated bonding

	Ceramic YAG	Qx/Er Phosphate Glass
Bulk Material	15.1 kg	2.3kg
CADB Bonded	12.6kg	1.9kg
% of bulk strength	83%	83%

Ref: Traggis, etc, : Proceeding of 11th Annual Directed Energy symposium, DEPS (2008)

Summary

- State of the art Konoshima's transparent ceramics were demonstrated.
- transparent ceramic is suitable for laser,scintillator, Farady materials
- perfomance of ceramic,as laser scintilltor material, is higher than that of tradtional single-crystal material
- composite material with high mechanical properties,low deffects.by using ceramic bonding thnique

Scintillator materials

Scintillator materials are widely used for application of high-energy physics, medical imaging.

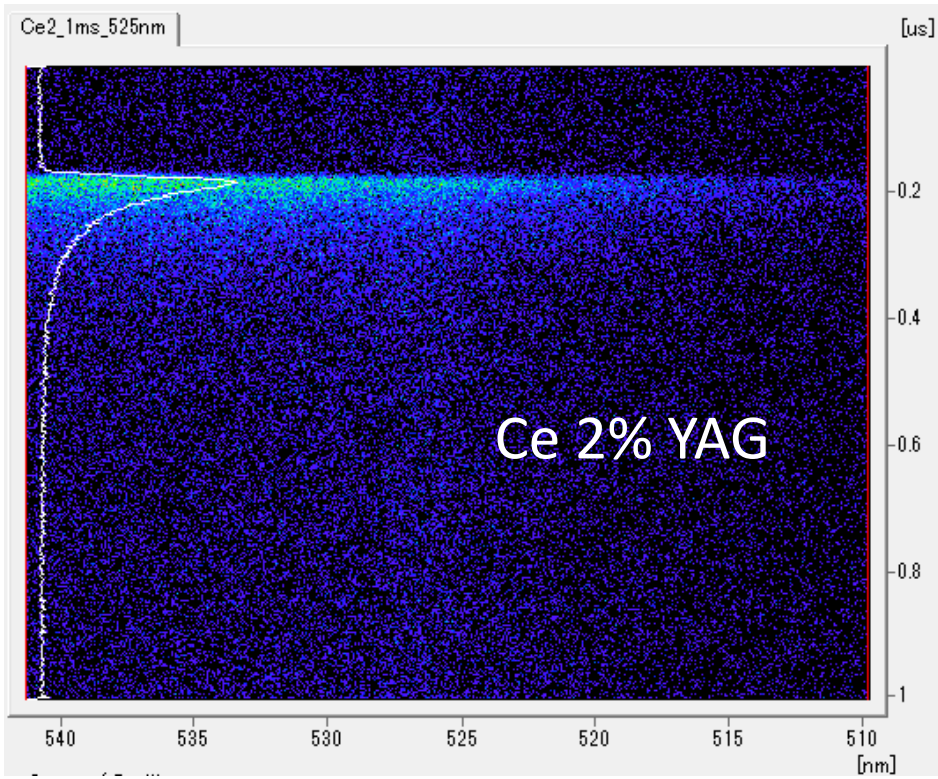
They require
- High light yield (output)
- Fast decay time
- High density, easy fabrication, low cost

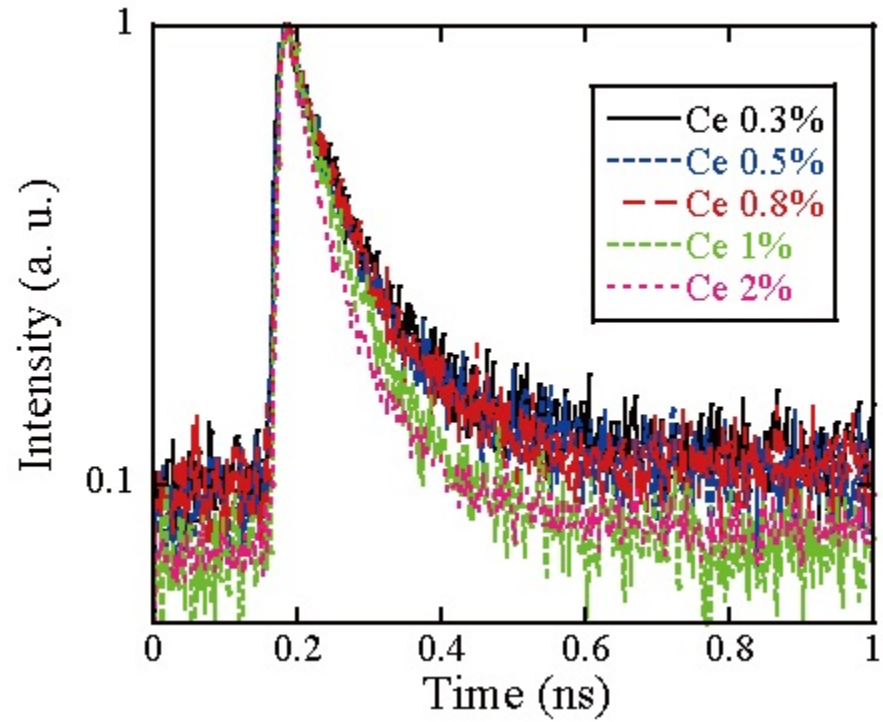
Physical properties of typical scintillator crystals

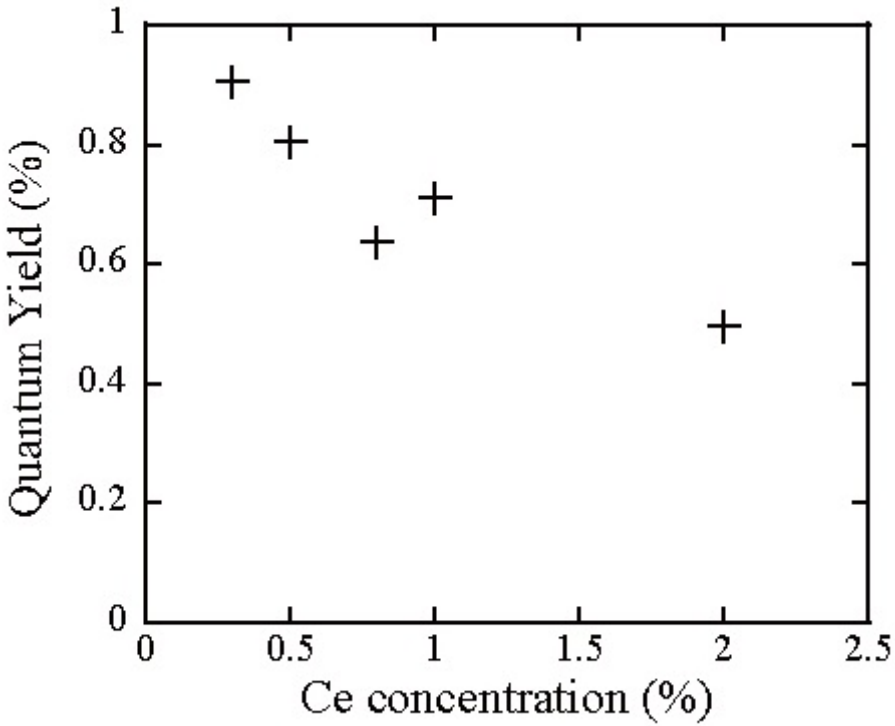
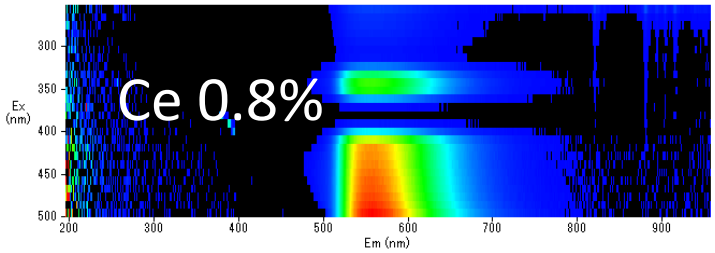
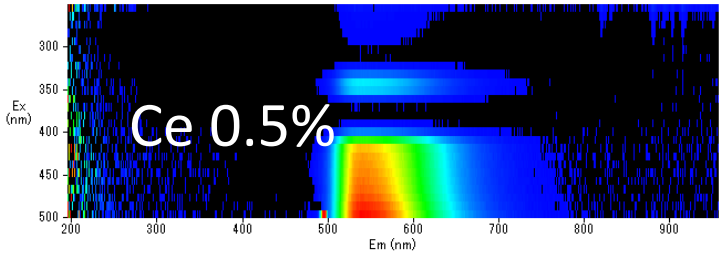
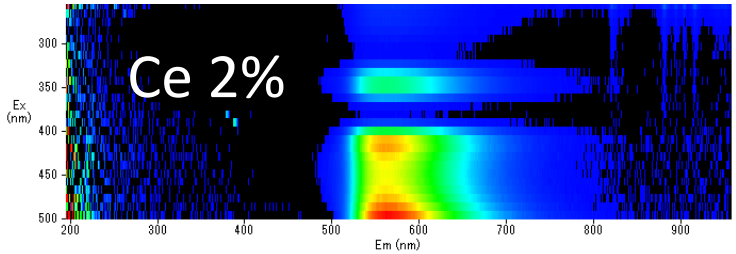
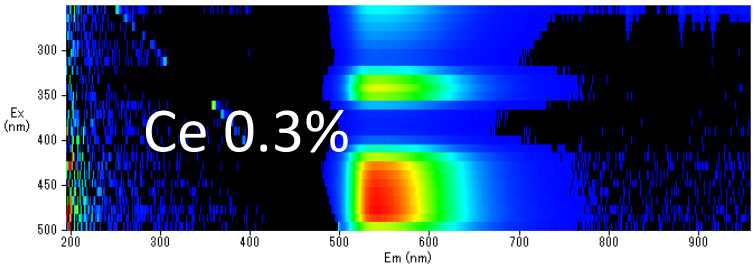
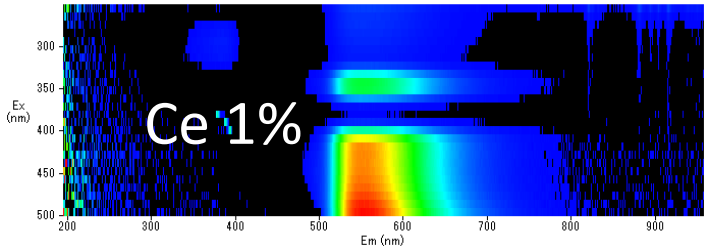
	BGO	Ce:GSO	Ce:LSO	Pr:LuAG	Ce:LuAG	Ce:YAG
density (g/cm3)	7.13	6.7	7.4	6.7	6.7	4.5
light yield (ph/MeV)	8600	8000	26000	18000	12500	24000
decay time (ns)	300	60	40	20	55	90
emission wavelenth (nm)	480	420	390	310	530	550
melting point (℃)	1050	1950	2150	1950	1950	1950

LuAG is an excellent candidate for new scintillator material.
Especially, ceramic LuAG has several advantages compared with the single-crystal, such as scalability, uniform and highly doping.

Decay time measured by pulse X-ray streak





X-ray excited time & wavelength resolved streak image
(T. Yanagida et al., Appl. Phys. Express, vol.3 ,056202 2010)

PL absolute Quantum yield of YAG:Ce