Fabrication of rare-earth doped sesquioxide laser ceramics

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Nanyang Technological University

Singapore

Map of SINGAPORE
Malaysia
Malaysia
NANYANG TECHNOLOGICAL UNIVERSITY
NS11 Sembawang
NS10 Admiralty
NS9 Woodlands
NS8 Marsiling
NS7 Kranji
NS13 Yishun
NS14 Khatib
NS5 Yew Tee
NS4 BP1 Choa Chu Kang
NS15 Yio Chu Kang
NS16 Ang Mo Kio
NS3 Bukit Gombak
NS2 Bukit Batok
NE17 Punggol
NE16 STC Sengkang
NE15 Buangkok
NE14 Hougang
NE13 Kovan
EW1 Pasir Ris
CG2 Changi Airport
EW2 Tampines
EW3 Simei
CG1 Expo
EW4 Tanah Merah
EW5 Bedok
EW6 Kembangan
EW7 Eunos
EW8 Paya Lebar
EW9 Aljunied
EW10 Kallang
EW11
Dakota
Stadium Mountbatten
EW12
EW13
EW14 NS26 Raffles Place
EW15 Tanjong Pagar
NS27 Marina Bay
EW16 NE3 Outram Park
EW17 NE5
EW18 Redhill
EW19 Queenstown
EW20 Commonwealth
EW21 Buona Vista
EW22 Dover
EW23 Clementi
EW24 NS1 Jurong East
EW25 Chinese Garden
EW26 Lakeside
EW27 Boon Lay
EW28 Pioneer
EW29 Joo Koon
CC10 MacPherson
CC11 Tai Seng
CC12 Bartley
CC13 NE12 Serangoon
CC15 NS17 Bishan
CC17 Thomson
CC18 Bukit Brown
CC19 Botanic Garden
CC20 Farrer Rd
CC21 Holland Village
CC22
CC23 One North
CC24 Kent Ridge
CC25 West Coast
CC26 Pasir Panjang
CC27 Labrador Park
CC28 Telok Blangah
CC29 NE1 HarbourFront
CC4
NS18 Braddell
NS19 Toa Payoh
NS20 Novena
NS21 Newton
NS22 Orchard
NS23
NS24 NE6 Dhoby Ghaut
NE7
NE4
NE9 Boon Keng
NE10 Potong Pasir
NE8 Farrer Park
Lor Chuan
Marymount Rd
SINGAPORE MRT/LRT
North South Line
East West Line
North East Line
Circle Line (under construction)
Bukit Panjang LRT
Sengkang LRT
Punggol LRT

~ 700 km²

NTU campus

Facts about NTU

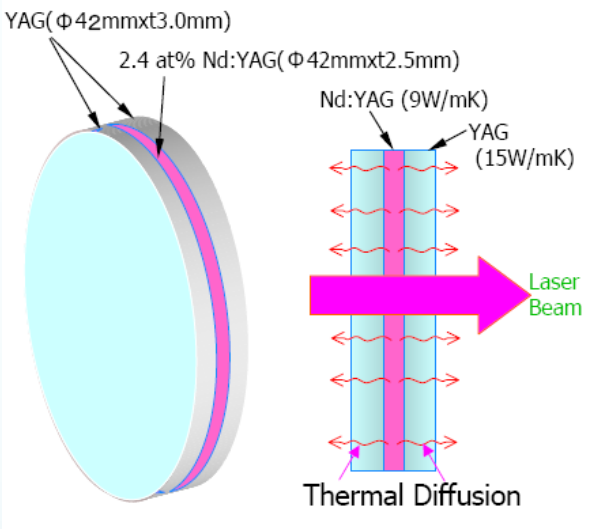
- Total student population – 33,478.
  - 23,481 undergraduates
  - 8,364 graduate students
- Students from 73 countries.
- Total staff strength – 5,930 (of which 3,100 are faculty and research staff from 67 countries).
- Ranked in top 100 universities in the world.

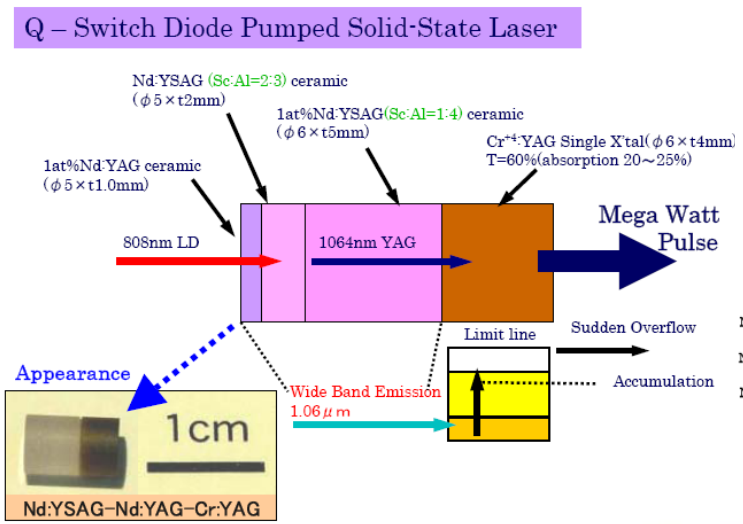
Outline

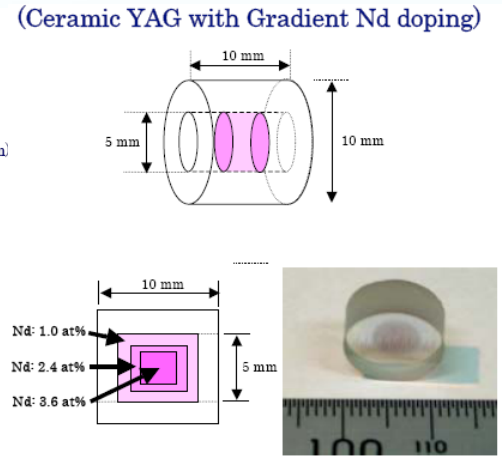
- Research background
- Fabrication of Er:Y_2O_3 laser ceramics
  - Fabrication process and parameter control
- Nd:Y_2O_3 , Yb:Lu_2O_3 and Nd:Lu_2O_3 laser ceramics
- Conclusions

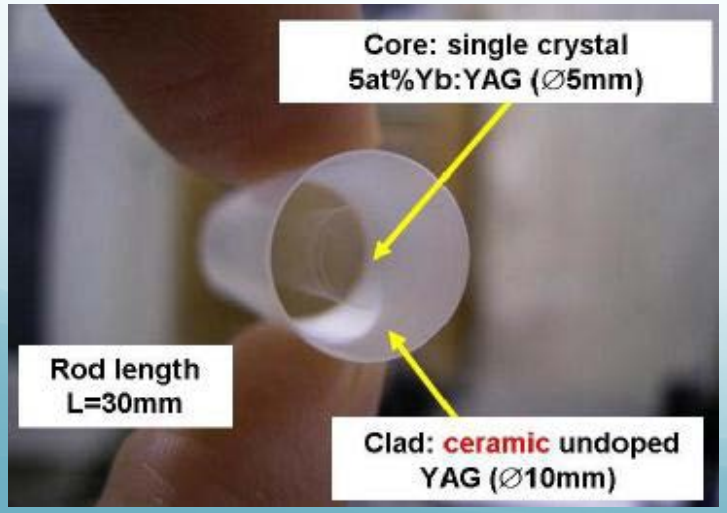
Advantages of ceramic laser gain media

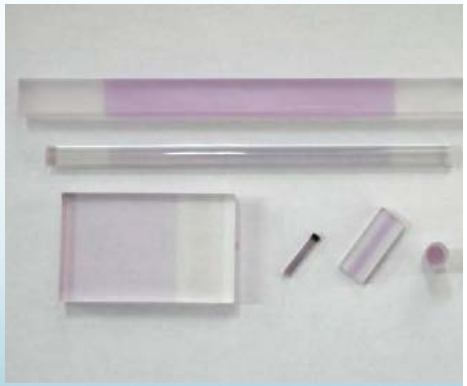
Large size, multilayer, flexible doping profiles, multifunctional …

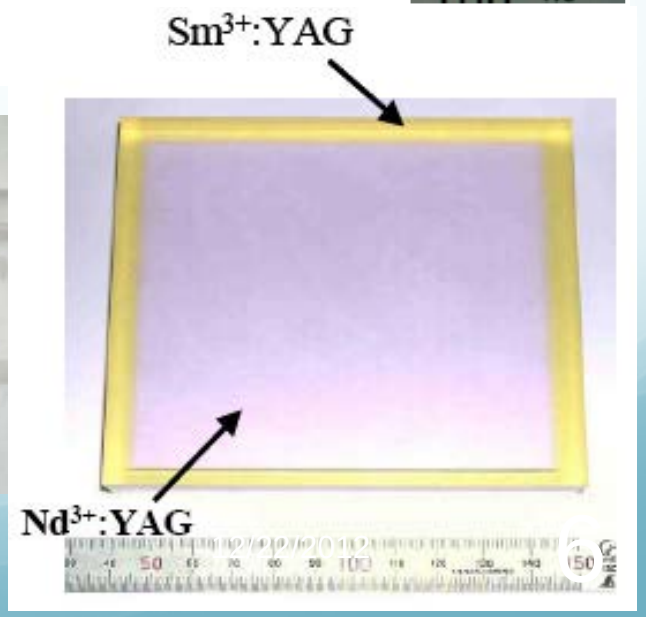






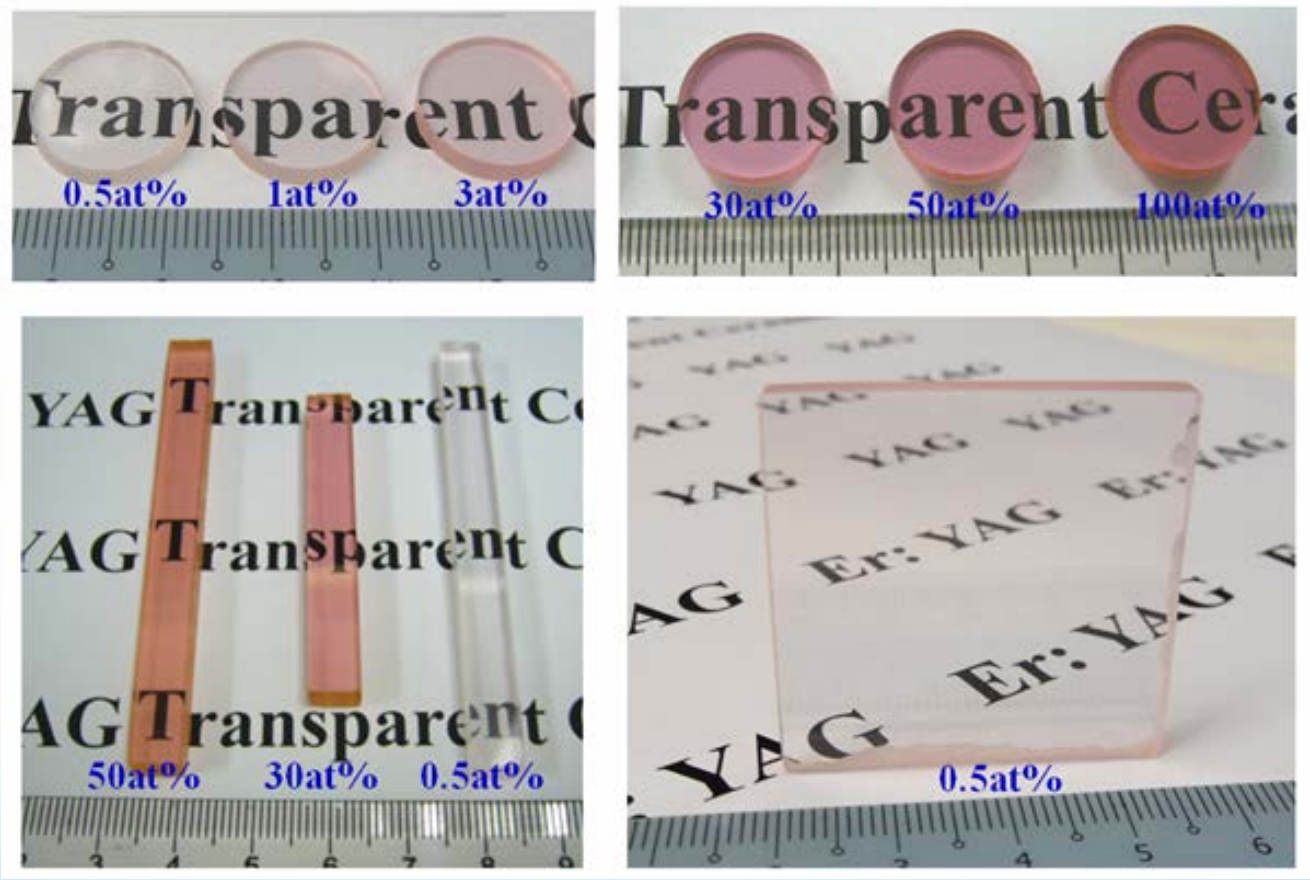






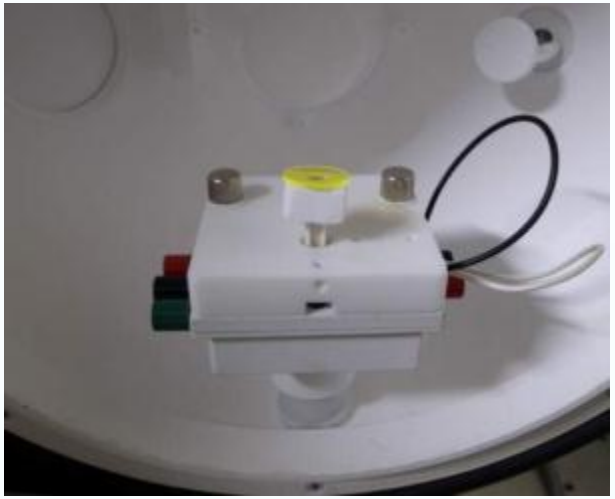
YAG based ceramics

Er:YAG ceramics fabricated in-house

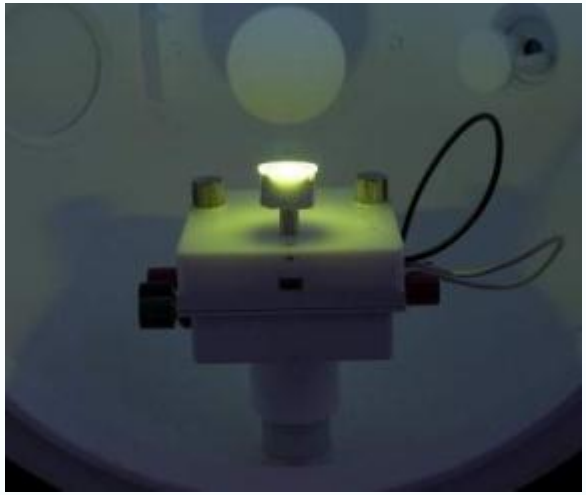


Different doping concentrations and size

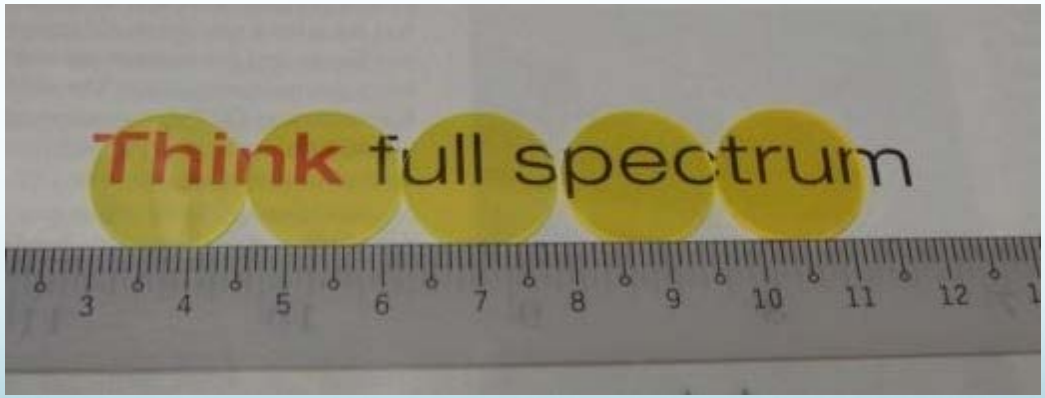
Ce:YAG ceramic phosphors



LED off



LED on



Advantages of sesquioxide laser gain media

- **Excellent mechanical and optical properties**
- **Large thermal conductivity**
- **Lower phonon energy than YAG**
- **Best candidate for high power lasers**

Table 1
Material properties of the high-melting sesquioxides compared to YAG

	Sc_2O_3	Y_2O_3	Lu_2O_3	YAG
Melting point (°C)	≈2430	2430	≈2450	1930
Structure	Cubic	Cubic	Cubic	Cubic
Space group	T_h^7	T_h^7	T_h^7	O_h^{10}
Site symmetry	C_2, C_{3i}	C_2, C_{3i}	C_2, C_{3i}	D_2, C_{3i}, S_4
Density of cation sites (10^{20} cm^{-3})	335.5	268.7	285.2	138
Lattice constant (Å)	9.844	10.603	10.391	12.00
Coordination numbers	6	6	6	8; 6; 4
Eff. ion-radius of the ion replaced by dopant (Å)	0.75	0.90	0.86	1.02
Thermal conductivity undoped (at 30°C) (W/mK)	16.5	13.6	12.5	11.0
Doped with 3% Yb (at 30°C) (W/mK)	6.6	7.7	11.0	6.8
Transparency range (μm)	0.22–?	0.23–8	0.23–?	0.18–6
Eff. phonon energy for RE-dopants (cm^{-1})	<625	430	<430	700
Mohs hardness	<6.8	6.8	≈7	8.5

*V. Peters et al. Journal of Crystal Growth, Vol. 237–239, pp 879–883, (2002)

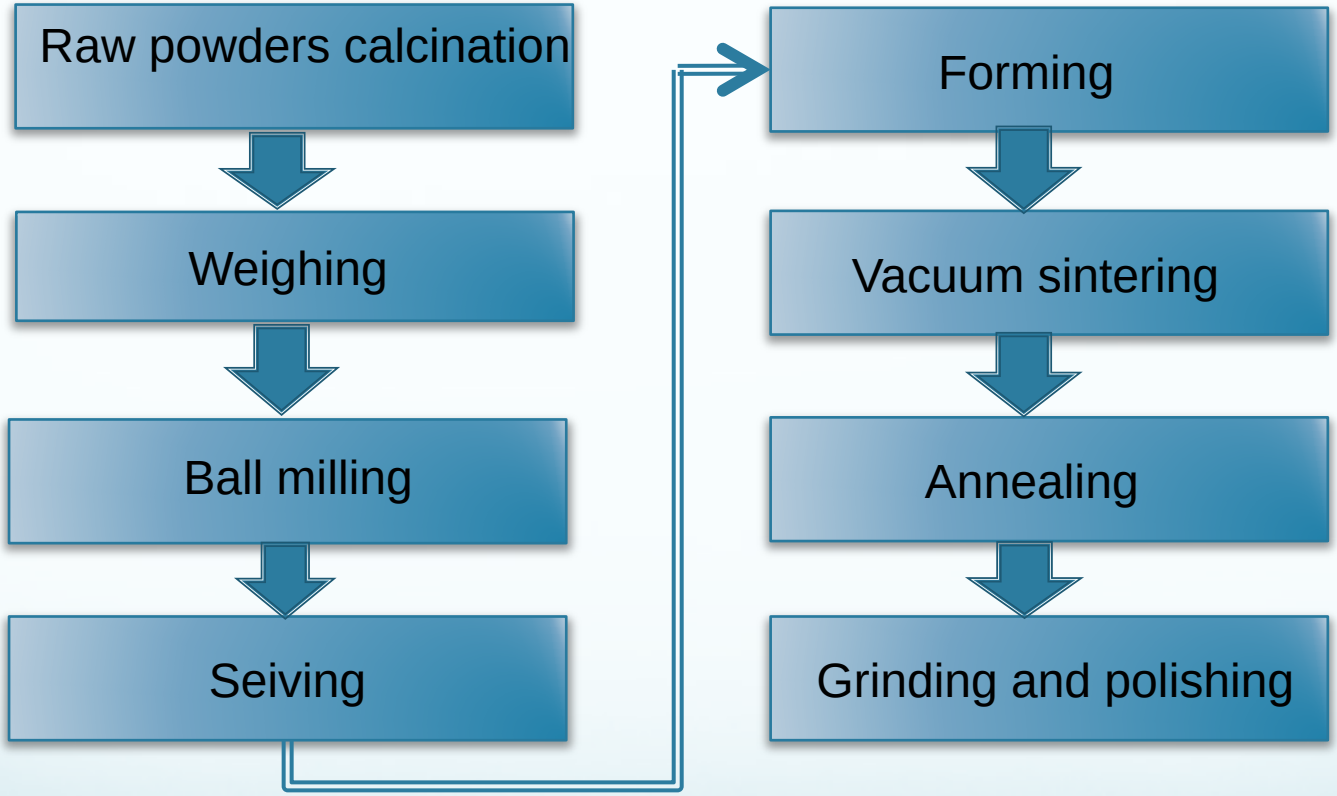
Advantages of sesquioxide laser gain media

- Excellent mechanical and optical properties
- Large thermal conductivity
- Lower phonon energy than YAG
- Best candidate for high power lasers

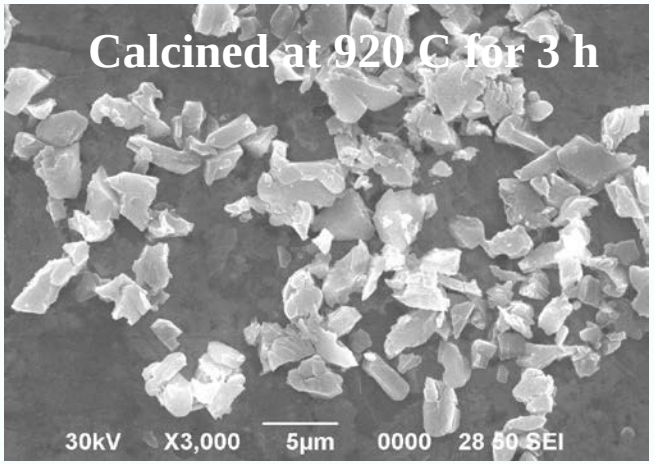
Extreme difficult to grow sesquioxide single crystals!

Fabrication of Er:Y_2O_3 laser ceramics

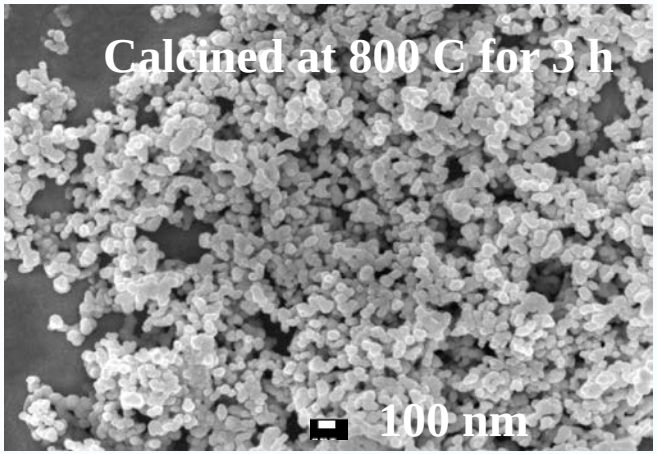
Flow chart of the fabrication process



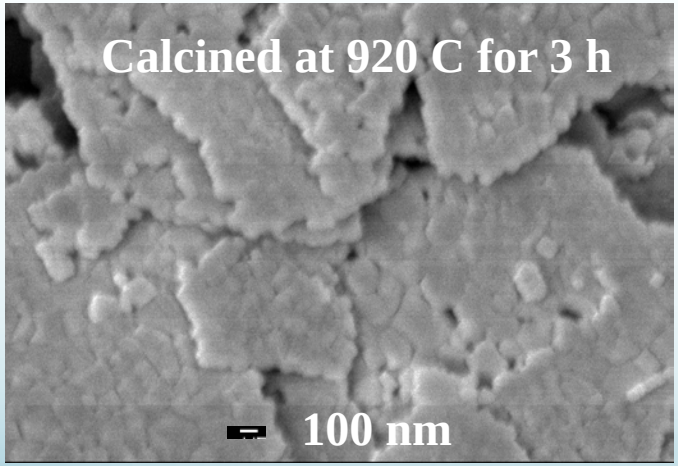
Raw powder selection



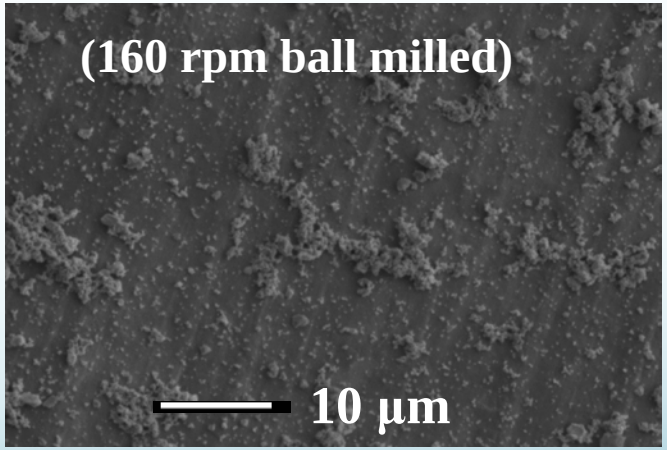
Y_2O_3 raw powders



ZrO_2 raw powders



Er_2O_3 raw powders



Mixed powders

Milling jars and ball selection

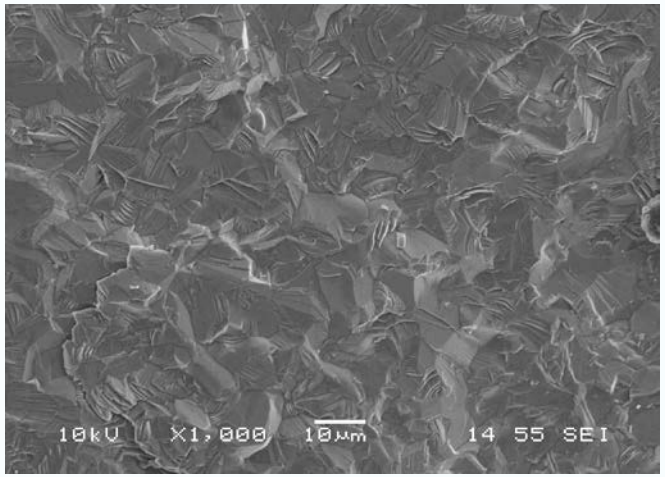
Cerium Stablized Zirconia (CSZ) jars

Yttrium Stablized Zirconia (YSZ) Balls

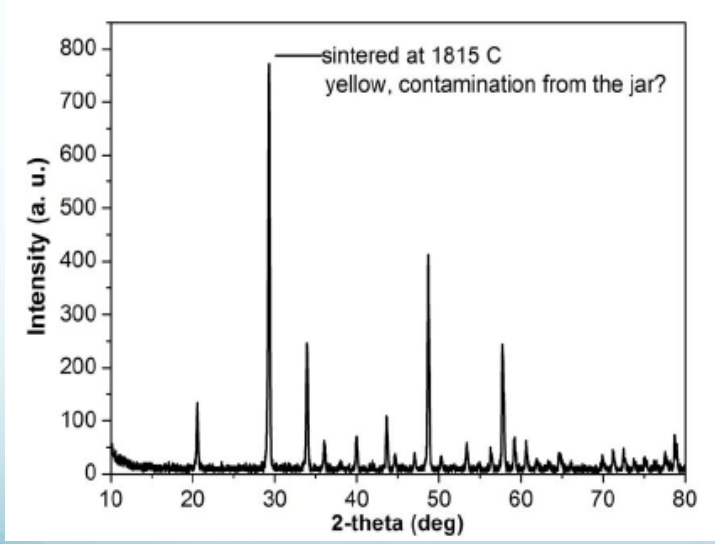
Nylon Jars

Alumina Balls

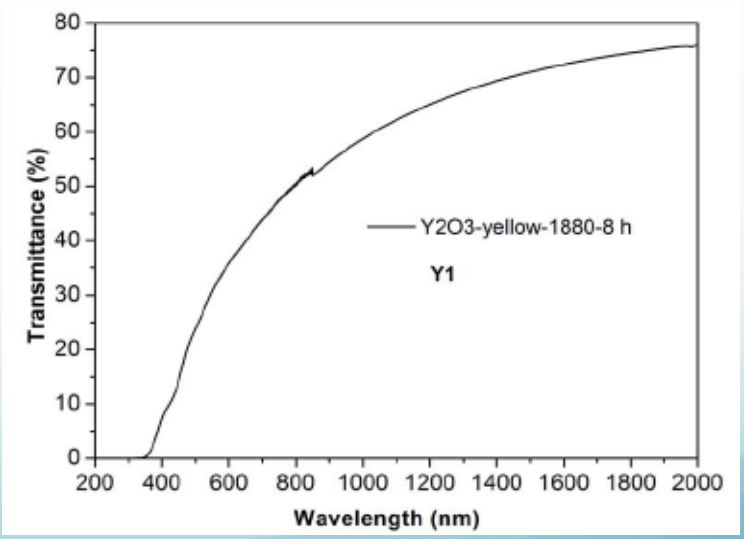
Results for CSZ jars and YSZ balls



SEM image



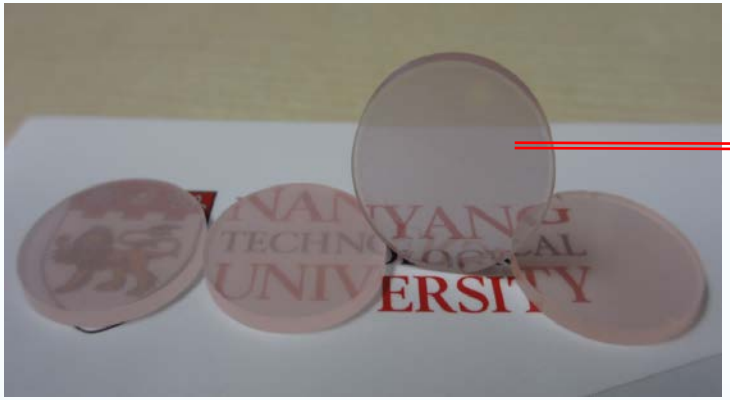
XRD spectrum

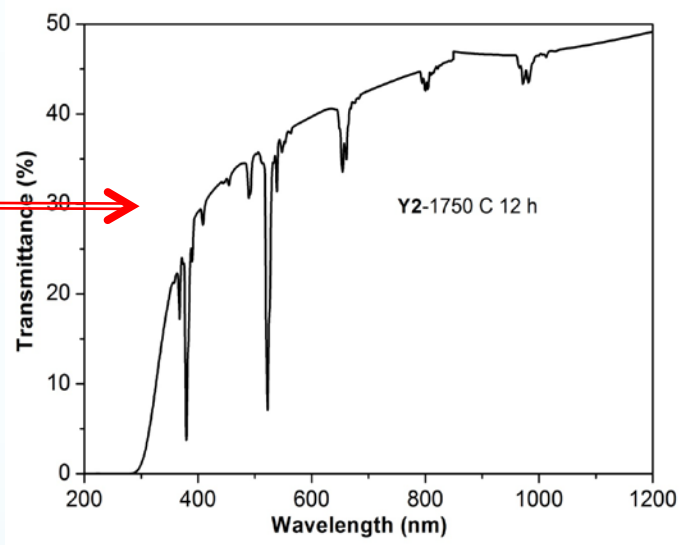


Transmission spectrum

Sintering aids selection

La, Zr, Hf were often used as the sintering aids in the early U.S. patents on fully densified Y_2O_3 ceramics.

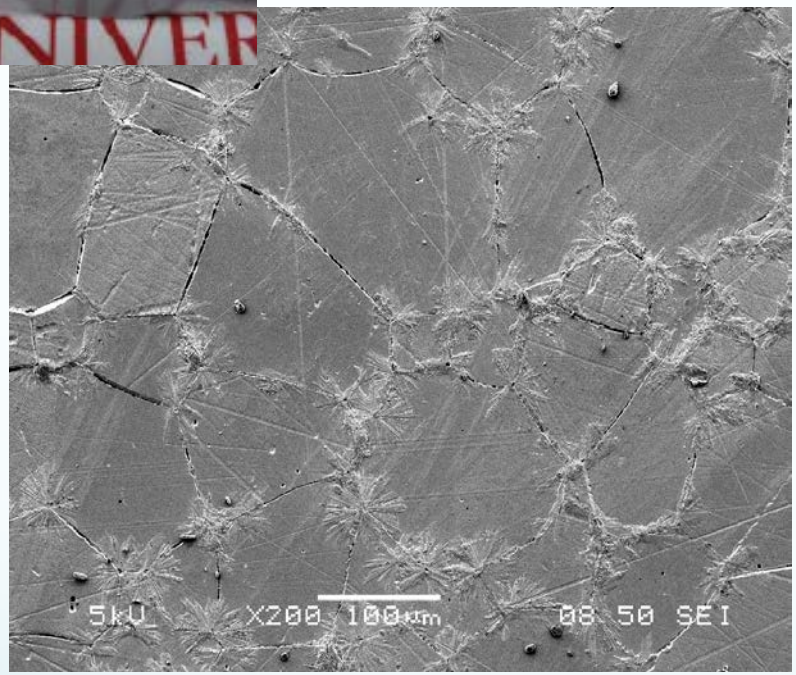


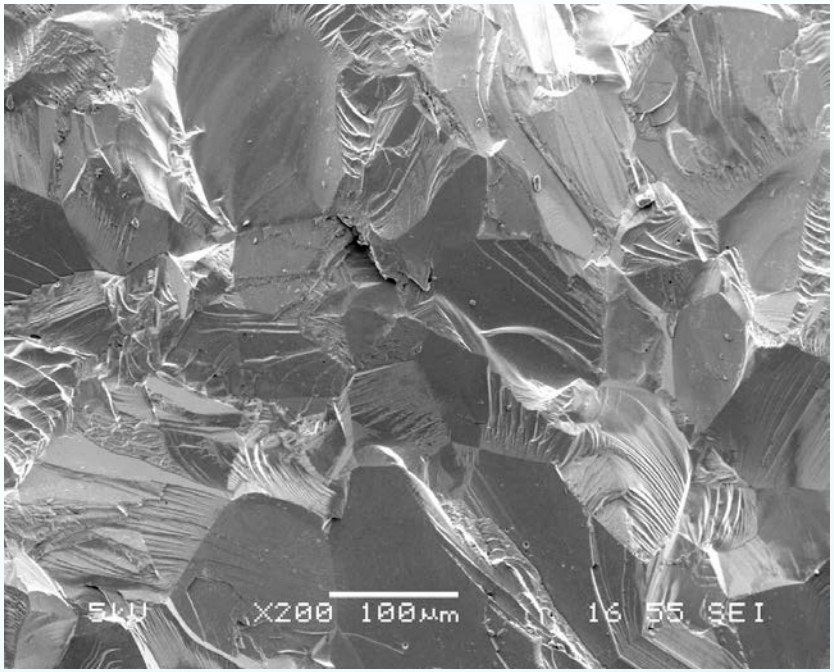


0.5 % Er: $(Y_{0.9}La_{0.1})_2O_3$ sintered at 1650 ℃, 1700 ℃, 1750 ℃ and 1815 ℃.

Towards $(Y_{1-x}La_x)_2O_3$ eramics with high optical quality,

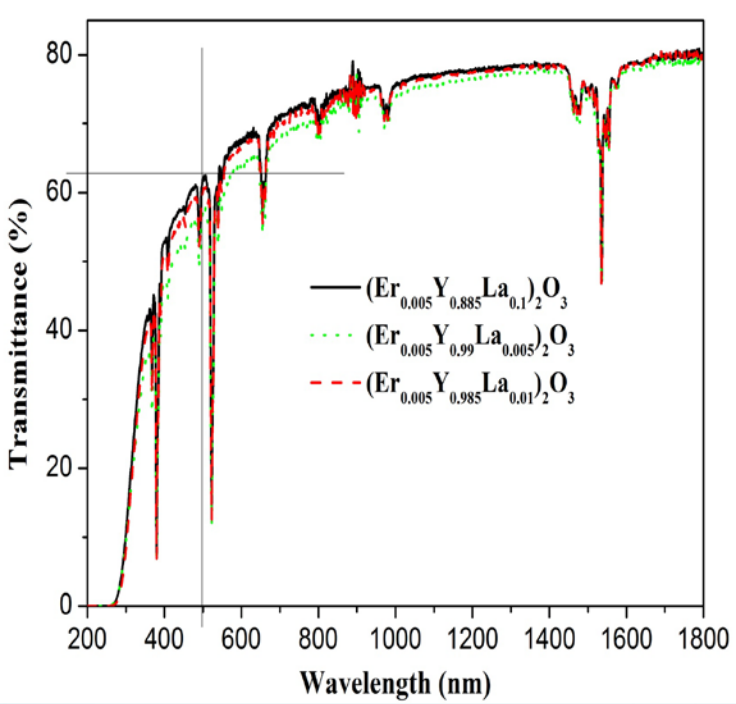
Sintering aids selection



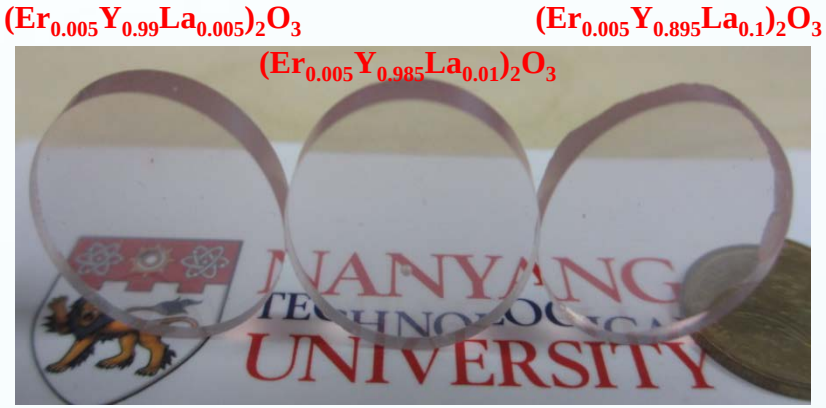


Y_2O_3 ceramics with 0.2 wt. % TiO_2 as the sintering aid, left: sinted at 1850 ℃ for 8 h; right: sintered at 1880 ℃ for 8 h. --- Abnormal grain growth.

Influence of sintering aids

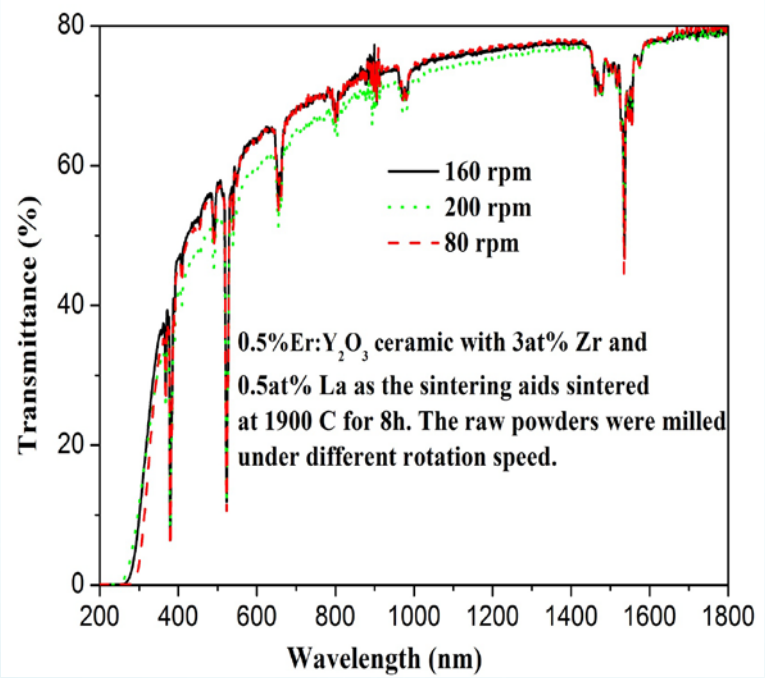


Measured transmission spectra

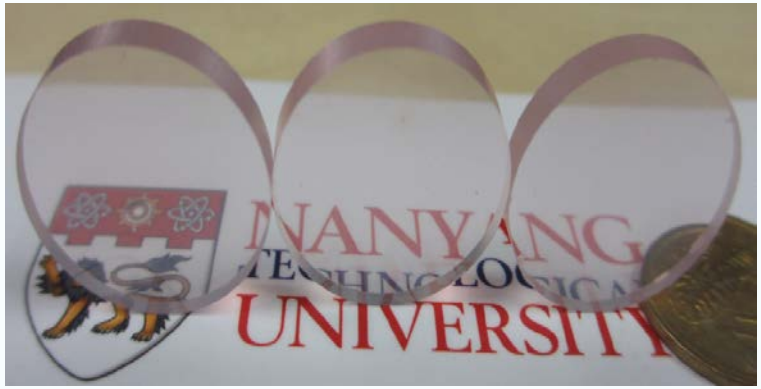


As-fabricated samples

Influence of the ball milling rotation speed

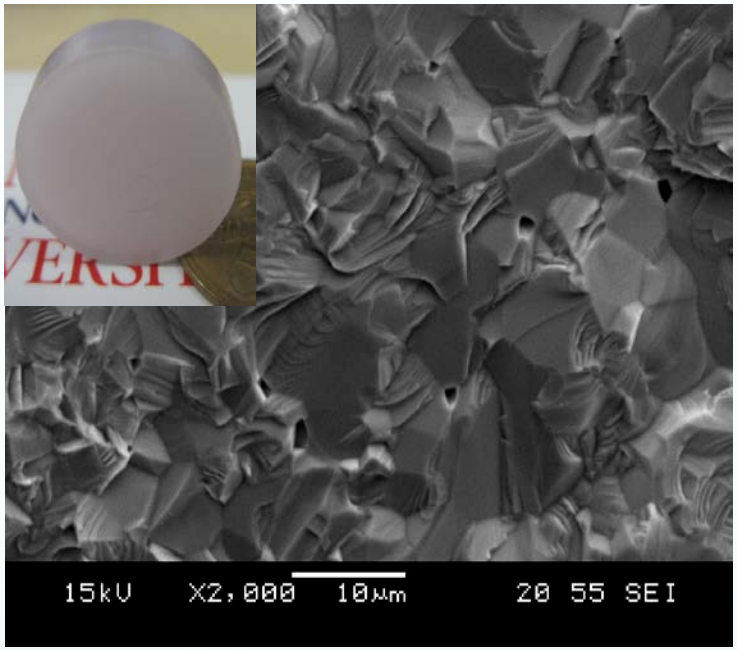


Measured transmission spectra



As-fabricated samples

Influence of the ball milling rotation speed



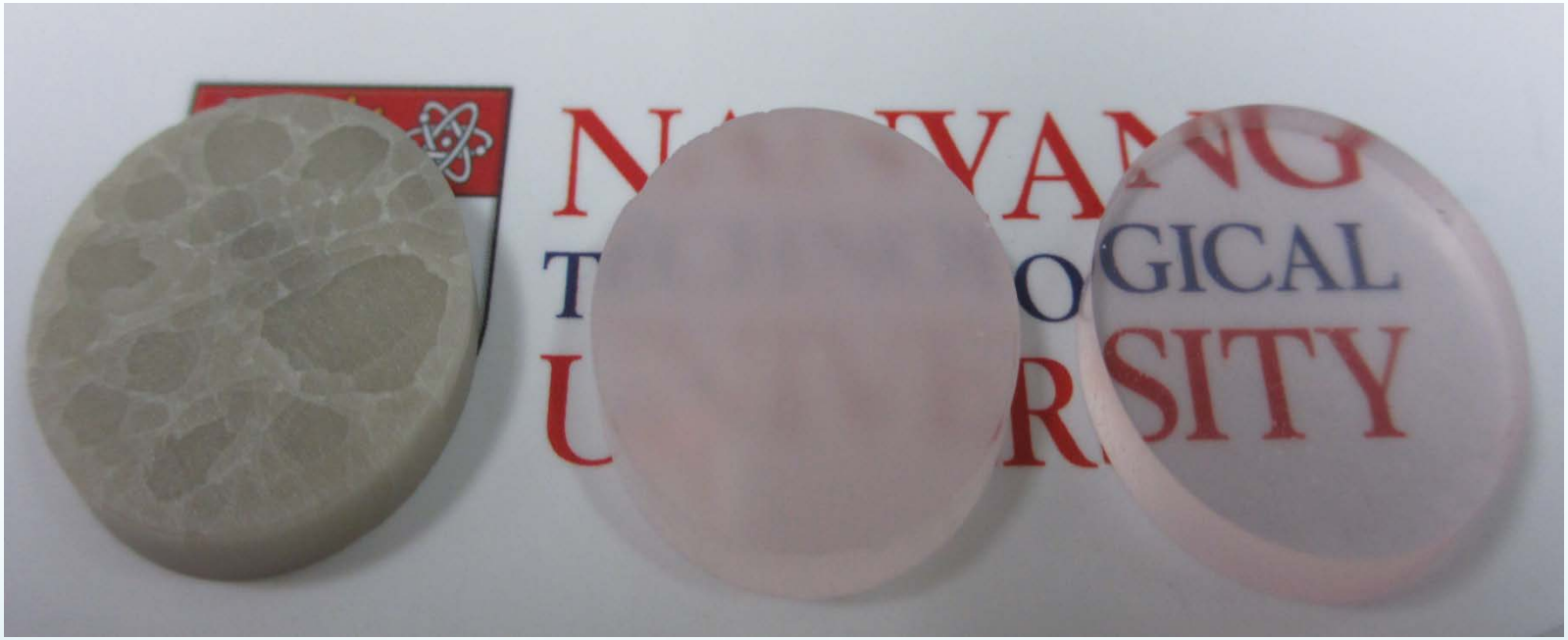
Too slow rotation speed (≤60 rpm) will cause inhomogeneous mixing. Samples are opaque and many residual pores are enclosed in the ceramics.

Influence of other effects

Cracking often occurred if the green bodies were kept for days. It was found due to the moisture absorption. Pre-sintering at a relatively high temperature (1000~1200 C) was needed for the single phase Y_2O_3 formation. The pre-sintering temperature should not be high to prevent obvious grain grown.

Towards cracking-free Y_2O_3 ceramics

Effect of Al_2O_3 as a sintering aid

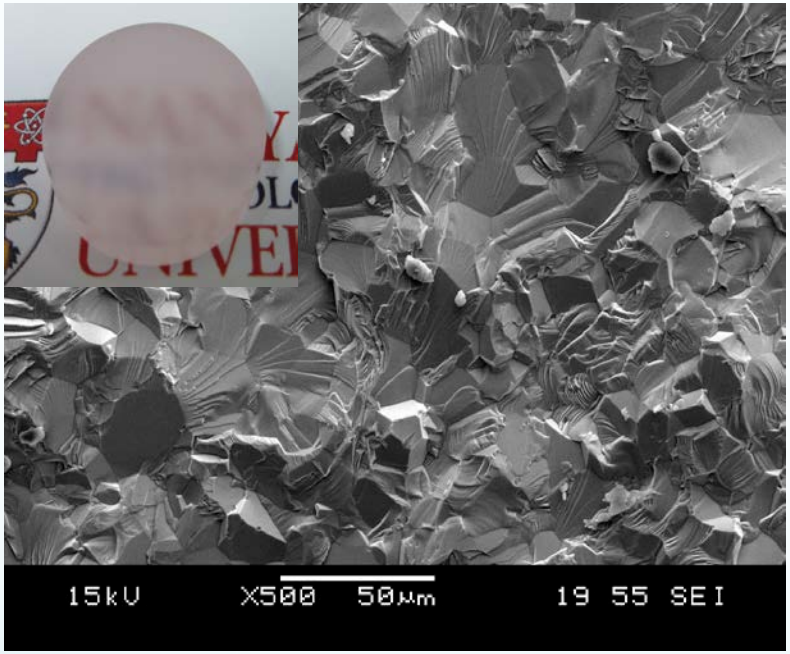


$(Er_{0.005}Y_{0.895}La_{0.1})_2O_3$ with 0.06 wt. % Al_2O_3

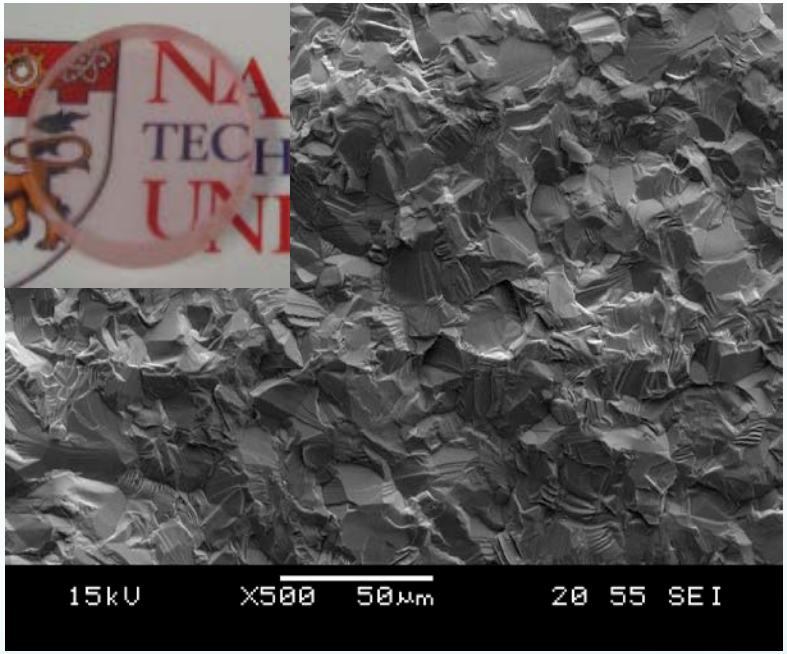
$(Er_{0.005}Y_{0.965}Zr_{0.03})_2O_3$ with 0.06 wt. % Al_2O_3

$(Er_{0.005}Y_{0.965}Zr_{0.03})_2O_3$ with no Al_2O_3

Morphology of the fracture surface

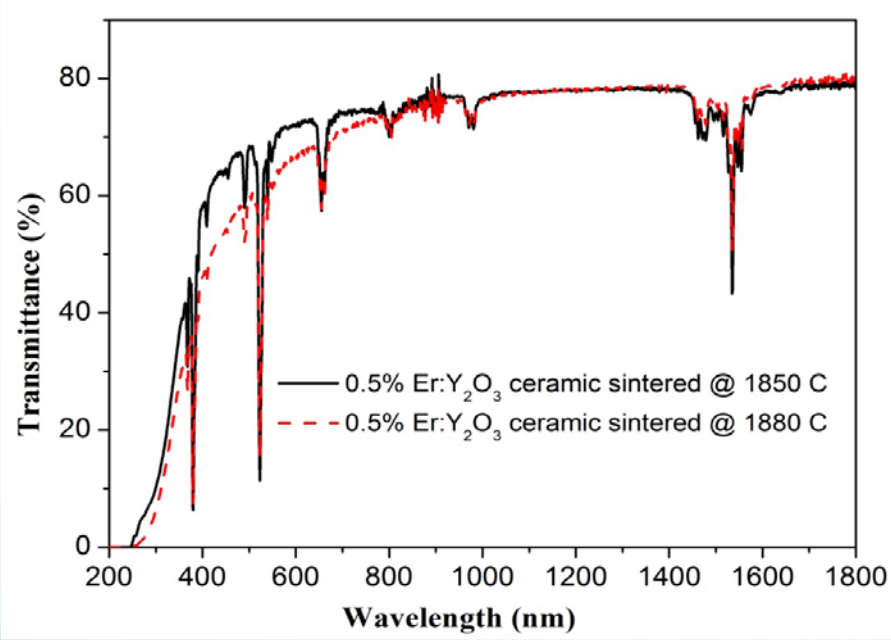


With Al2O3

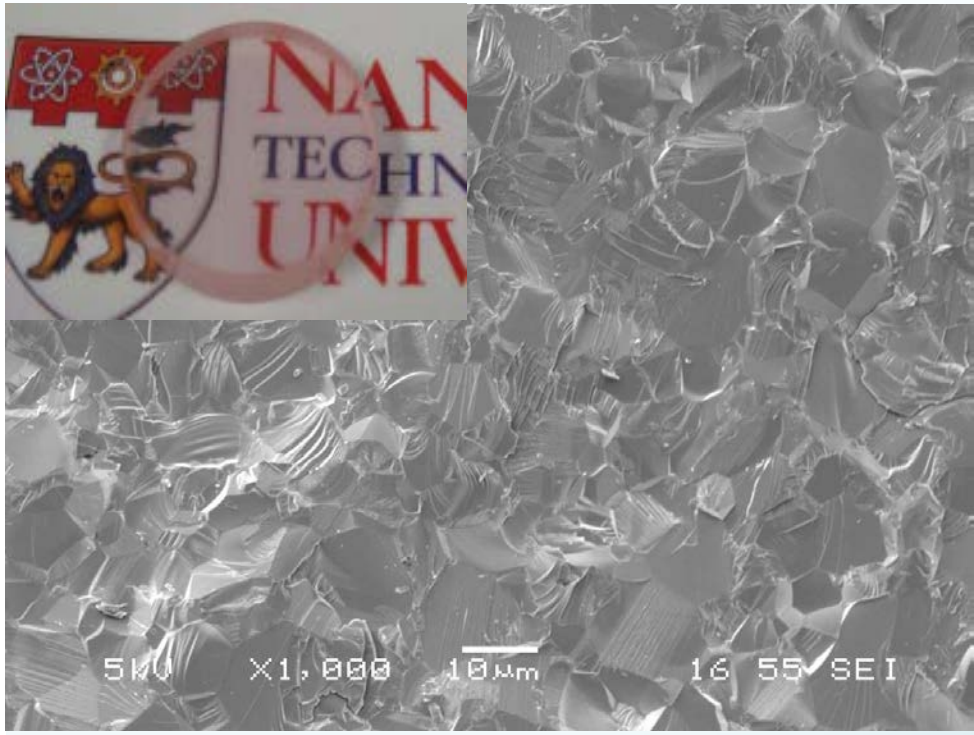


Without Al2O3

$Er:Y_2O_3$ samples fabricated in-house



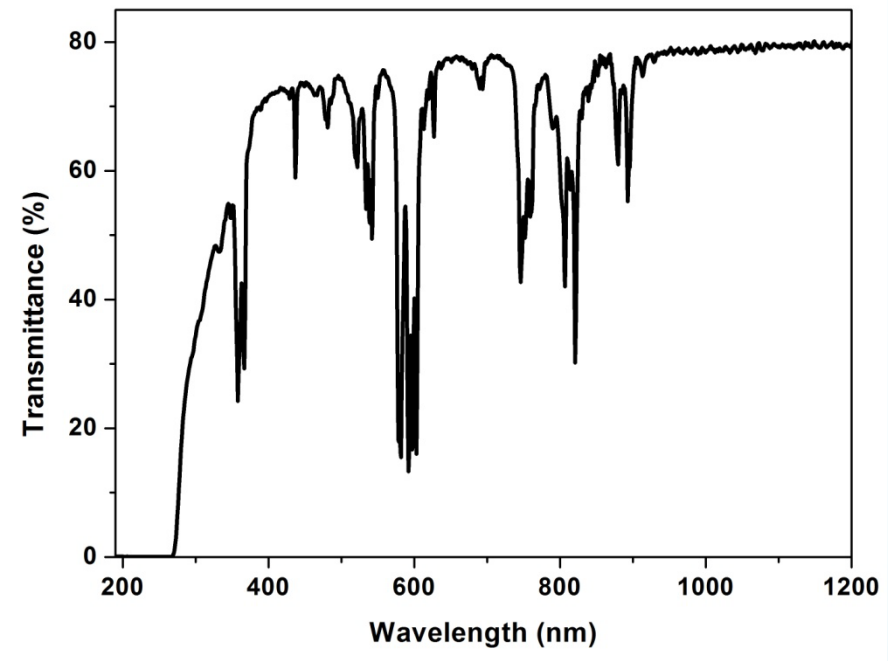
Transmission spectra



$Er:Y_2O_3$ ceramic with 3 at. % Zr as the sintering aid, thickness: 3.27 mm, sintered at 1850 ℃ for 8h; (right): thickness: 2.36 mm, sintered at 1880 ℃ for 8h.

Fabrication of Nd:Y_2O_3 ceramics

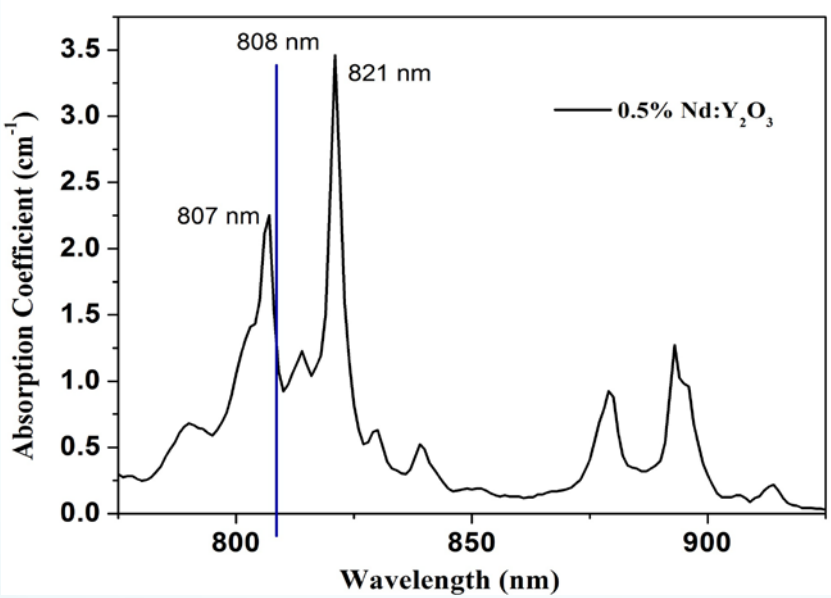
$Nd:Y_2O_3$ ceramics fabricated in-house

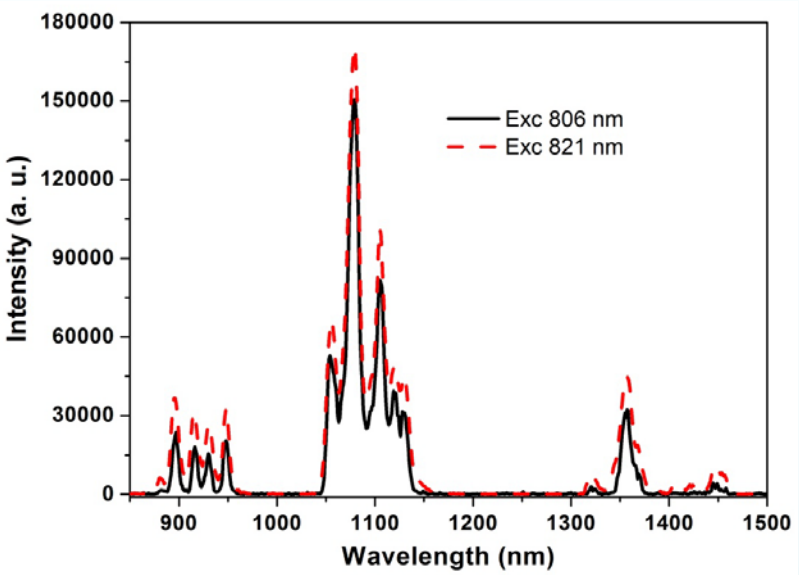


Optical transmittance of a 0.5 at. % $Nd:Y_2O_3$ ceramic

The as-fabricated $Nd:Y_2O_3$ sample

Absorption and emission spectra



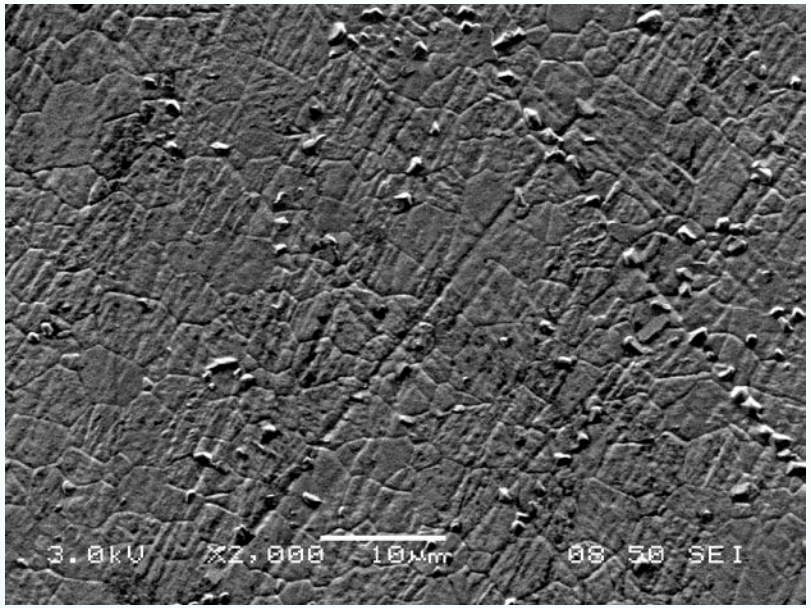


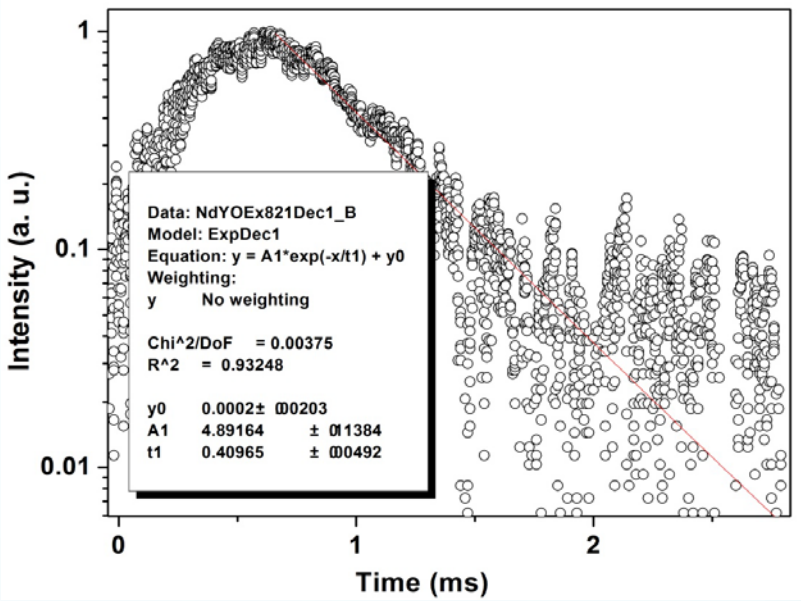
Absorption spectrum

Emission spectra under 806 nm and 821 nm excitation

3 at.% Zr was adopted as the sintering aid.

Grain structures and emission lifetime

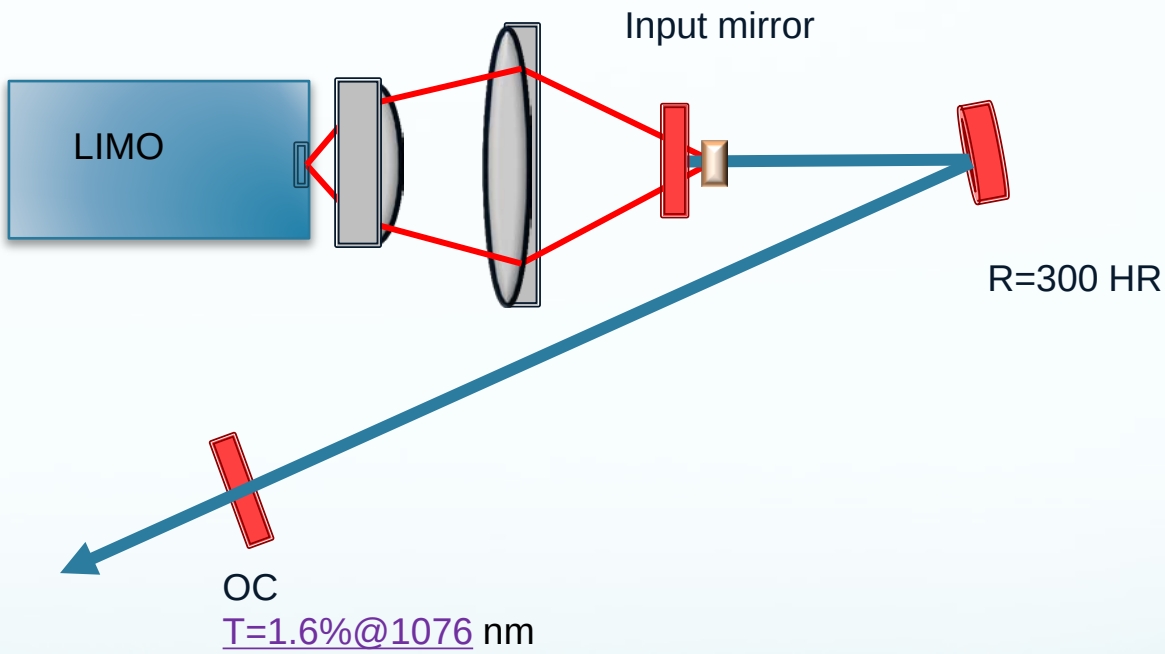




The average grain size is less than 10 µm, which is similar to that of the vacuum sintered YAG ceramics.

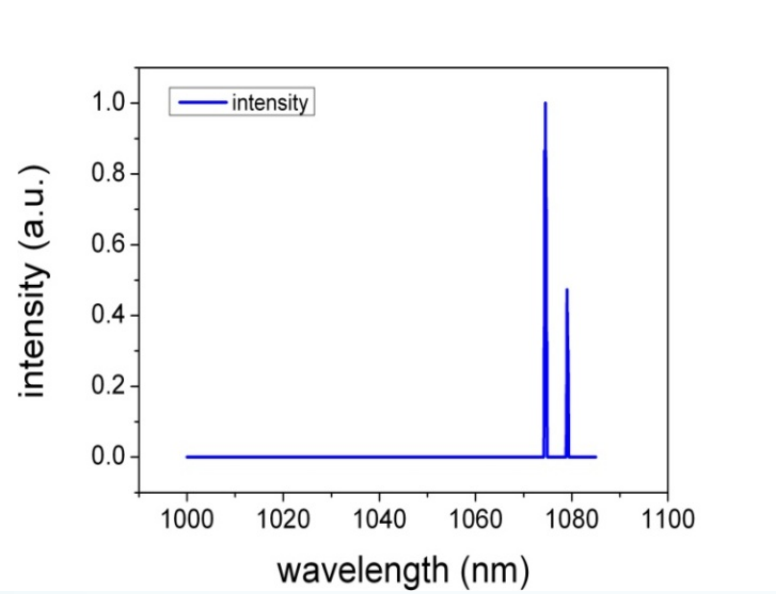
The measured 1078 nm emssion lifetime was ~400 µs (λ_{ex}=821 nm).

Laser experiment

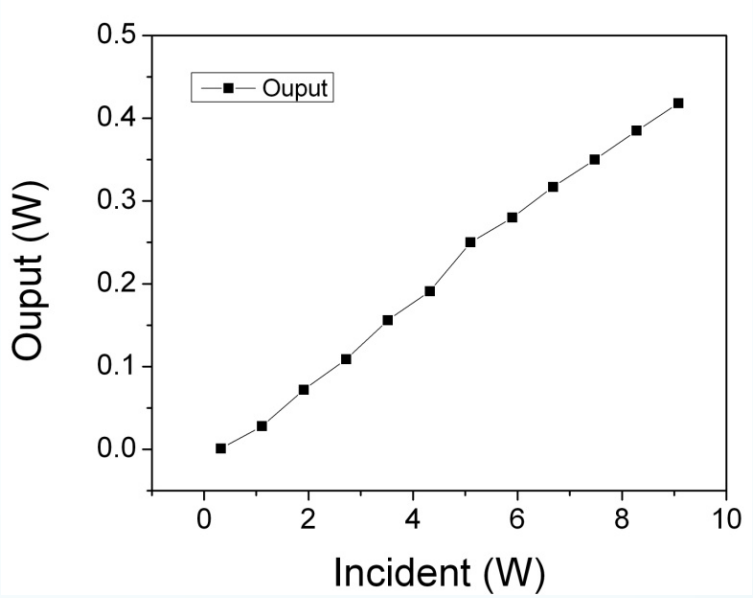


Experimental setup

Nd:Y_2O_3 ceramic laser performance



Emission spectrum

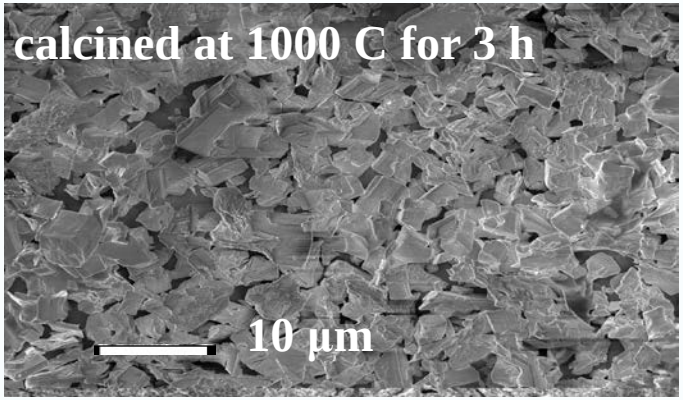


Laser performance

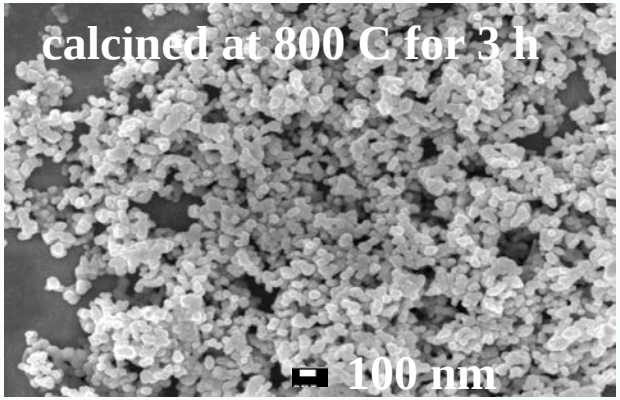
Dual wavelength CW laser oscillation has been achieved on our 0.5 at.% Nd:Y_2O_3 ceramic samples.

Yb^{3+} doped Lu_2O_3 ceramics

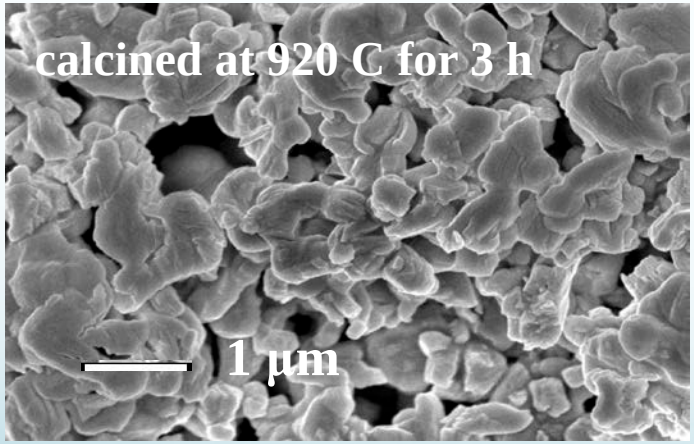
Raw powder selection



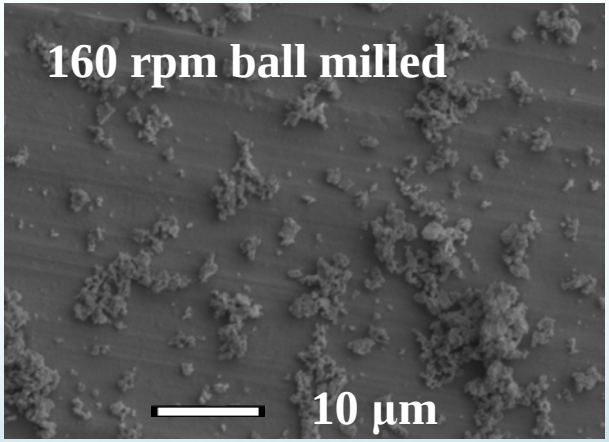
Lu_2O_3 powder



ZrO_2 powders



Yb_2O_3 powder



mixed powder

$Yb:Lu_2O_3$ ceramics fabricated in-house

1 2 3 4 5

1 7at%Yb:Lu2O3 with 3%Zr sintered at 1900 C

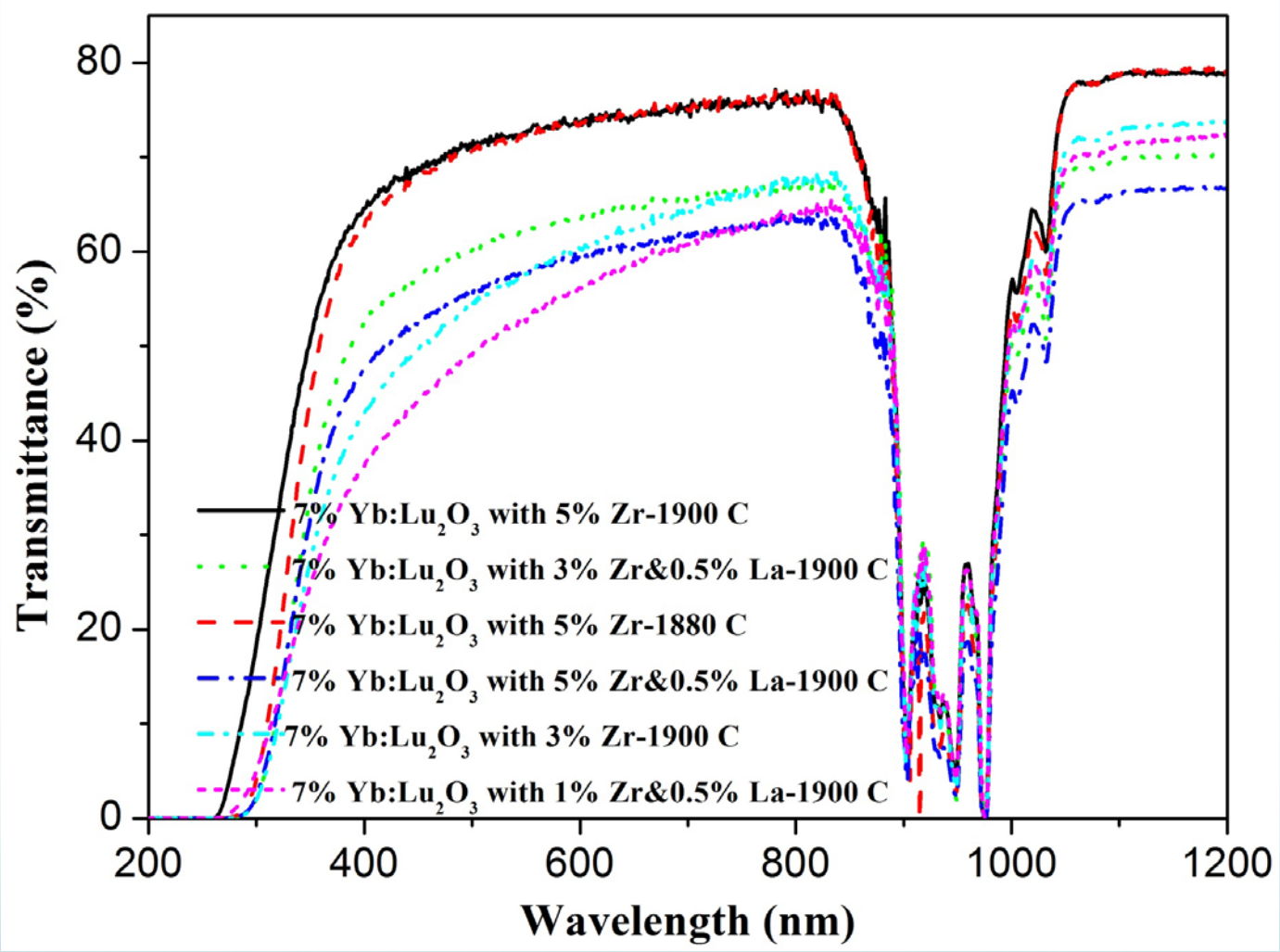
2 7at%Yb:Lu2O3 with 3%Zr & 0.5% La sintered at 1900 C

3 7at%Yb:Lu2O3 with 5%Zr sintered at 1880 C

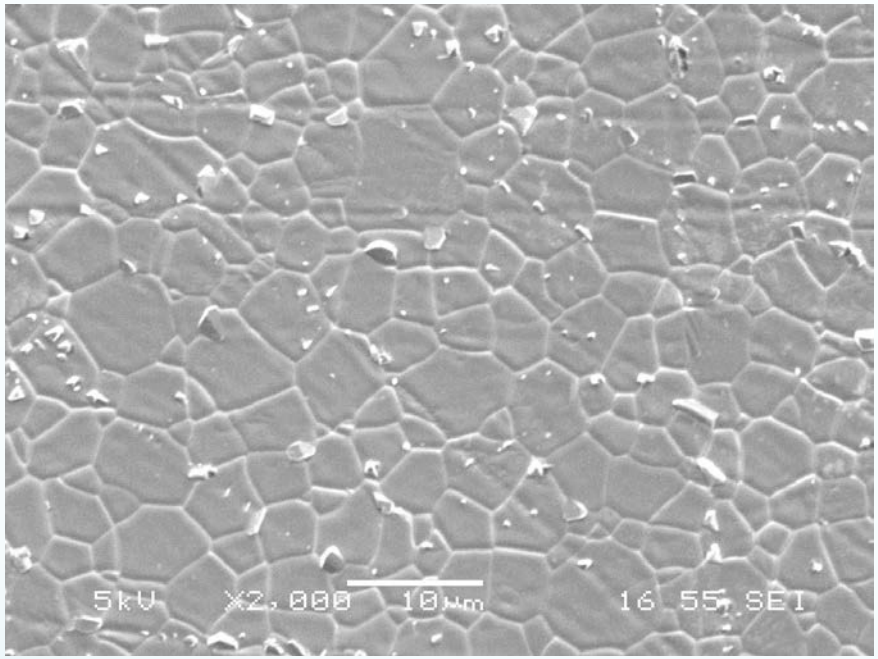
4 7at%Yb:Lu2O3 with 5%Zr sintered at 1900 C

5 7at%Yb:Lu2O3 with 1%Zr & 0.5% La sintered at 1900 C

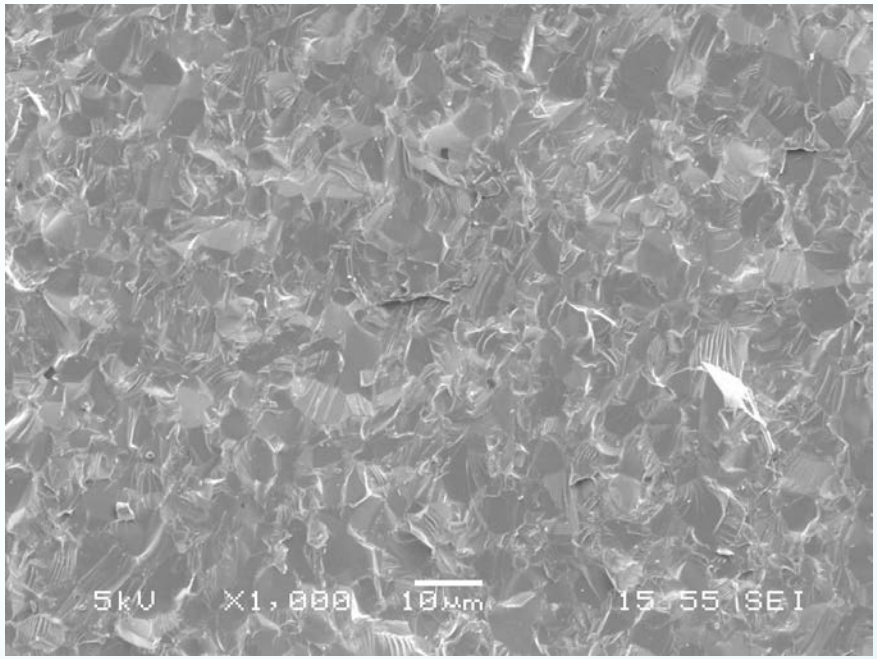
Influence of sintering aid



Transmission spectra measured



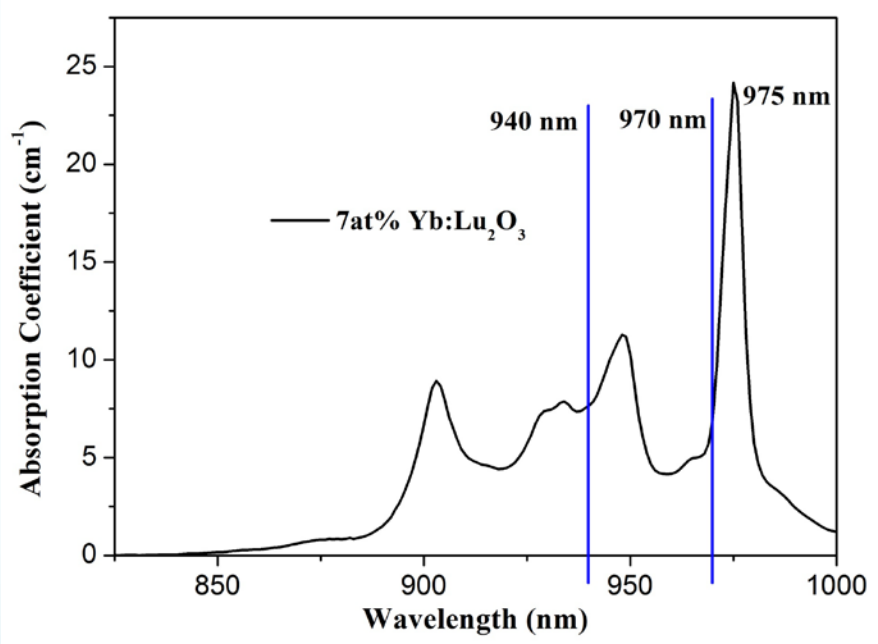
SEM morphology of the polished surface after thermal etching.



SEM morphology of fracture surface of the 7at%Yb:Lu2O3 ceramic.

The average grain size of the 7at%Yb:Lu2O3 ceramic is about 6 μm.

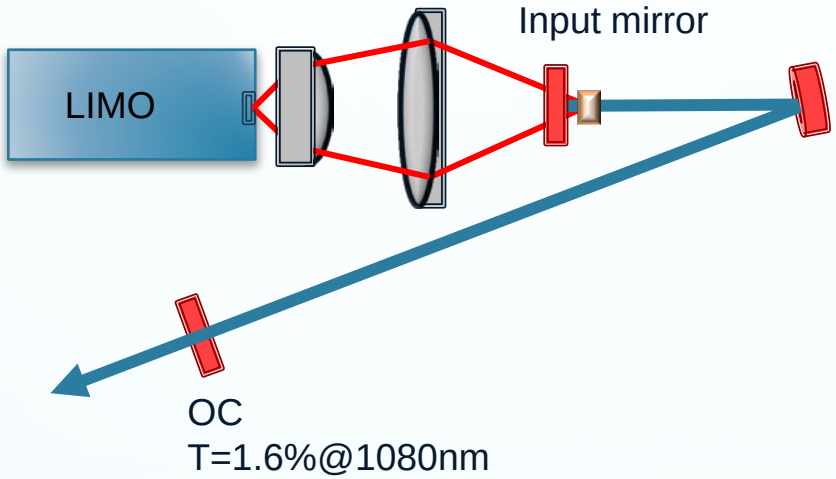
Absorption spectrum

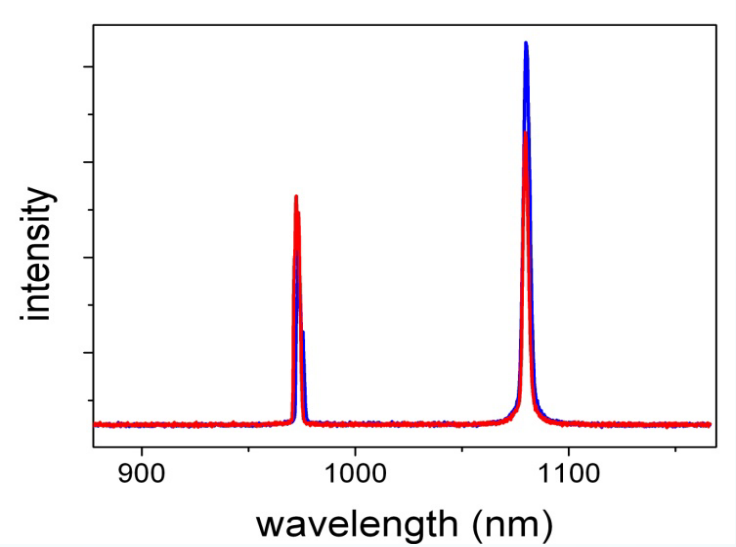


Yb:Lu_2O_3 sample

Absorption Spectrum of a 7at. % Yb:Lu_2O_3 ceramic.

Laser experiment



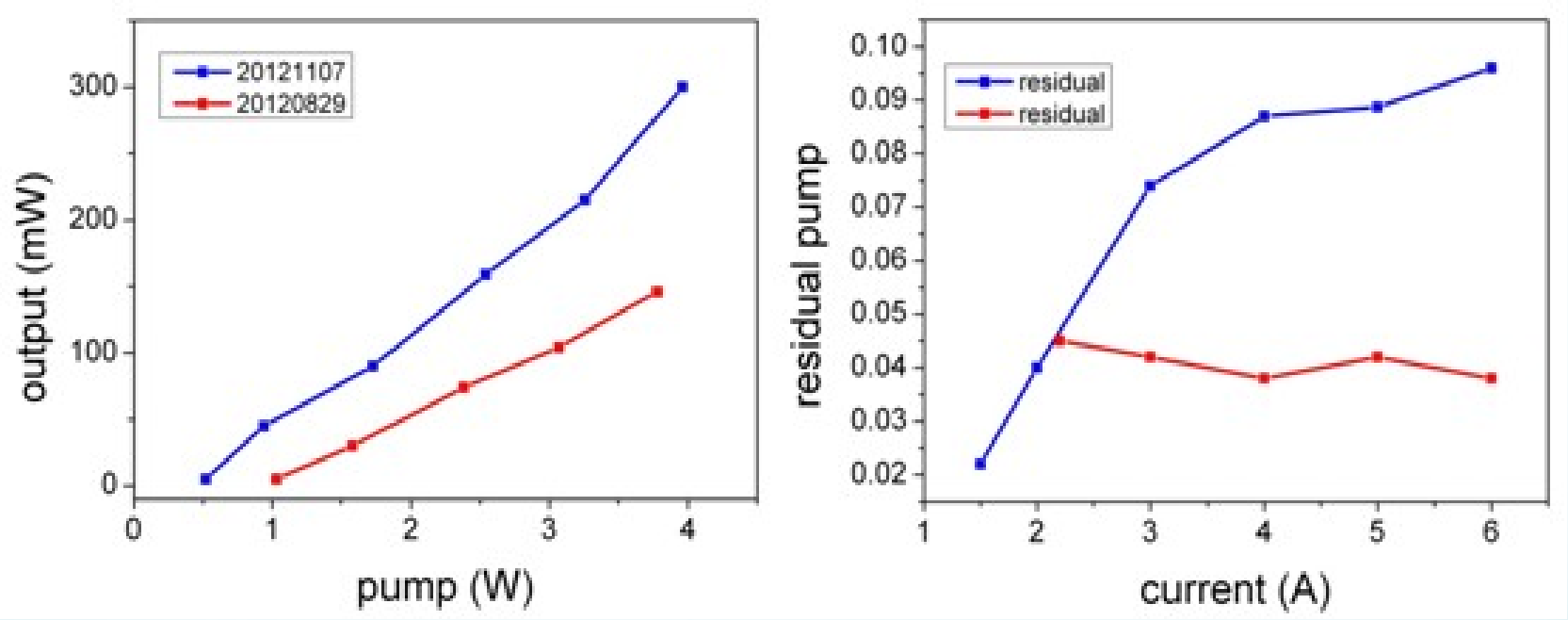


Pumping wavelength: 976nm
Emission wavelength: 1080nm

7at%Yb:Lu_2O_3 with 5at%Zr sintered at 1900 C for 8h

7at%Yb:Lu_2O_3 with 3at%Zr and 0.5at%La sintered at 1900 C for 8h

$Yb:Lu_2O_3$ ceramic laser performance

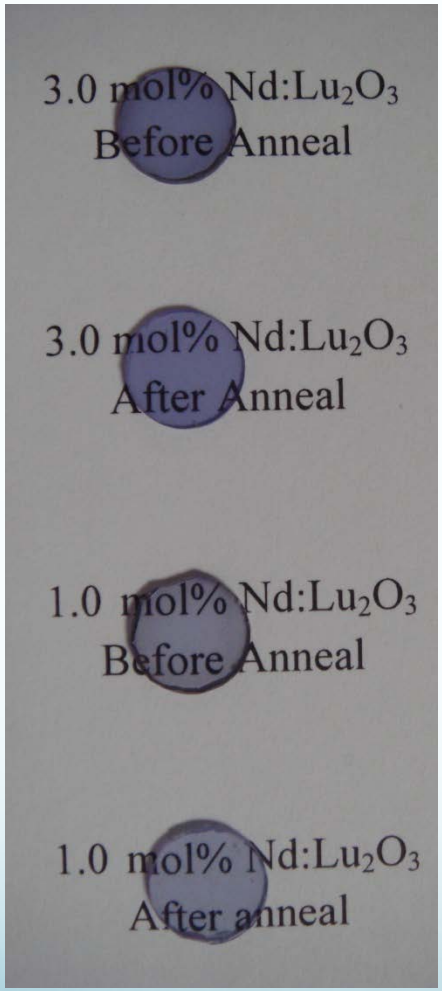


Laser performance **Residual pump features**

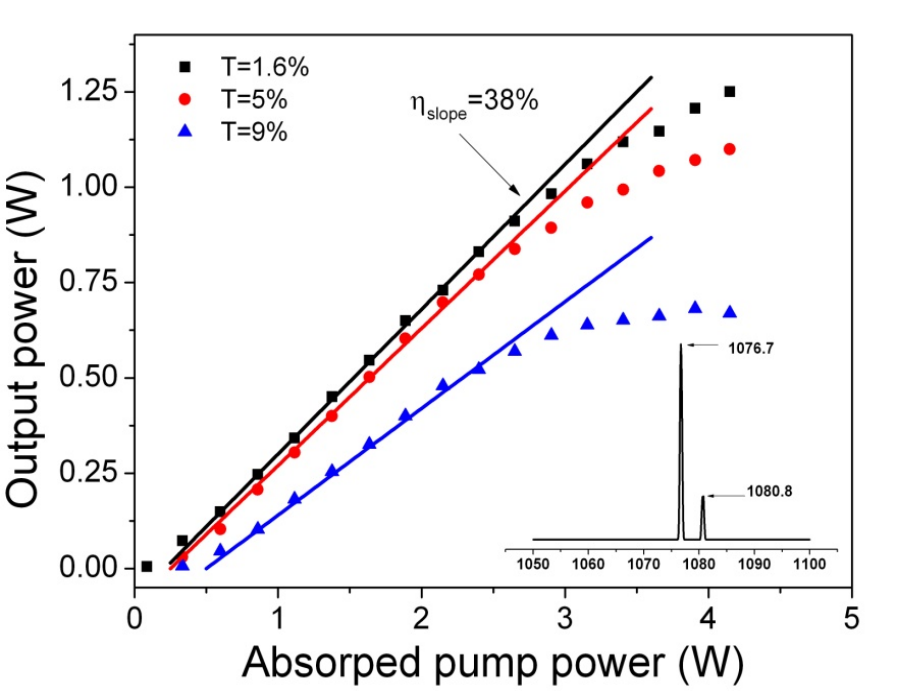
7at%$Yb:Lu_2O_3$ with 5at%Zr sintered at 1900 C for 8h

7at%$Yb:Lu_2O_3$ with 3at%Zr and 0.5at%La sintered at 1900 C for 8h

$Nd:Lu_2O_3$： SPS sintering method



1450 degree C for 5 min, pressure: 70 MPa



- Pump source： 808 nm LD
- Max output power： 1.25 W
- Slope efficiency: 38%
- Emission wavelength: 1076.7nm and 1080.8nm

Conclusions

- **The optimal process condition for fabricating transparent sesquioxide ceramics have been studied.**
- **Highly transparent Y_2O_3 and Lu_2O_3 ceramics have been produced.**
- **Laser oscillation on the Nd:Y_2O_3 ,Yb:Lu_2O_3 and Nd:Lu_2O_3 ceramics have been demonstrated.**
- **Further improvement on the optical quality of the ceramic are ongoing.**

From left to right:
0.5at%Nd:Y_2O_3, 0.5at%Ho:Y_2O_3, 0.5at%Er:Y_2O_3, 7at%Yb:Lu_2O_3

Thank You !