Winter School 2007 Kyoto

Laser Patterning of Crystals in Glass

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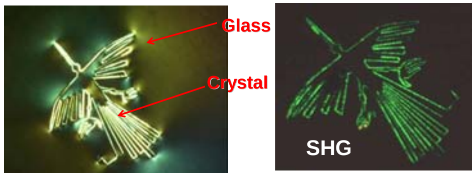
Plan of my talk

1. Basic concept of crystallization in glass
2. What is laser-induced crystallization (LIC)?
3. Patterning and Mechanism of LIC.



Glass

Key materials in information technology

↓

Glass Structure: Inversion Symmetry

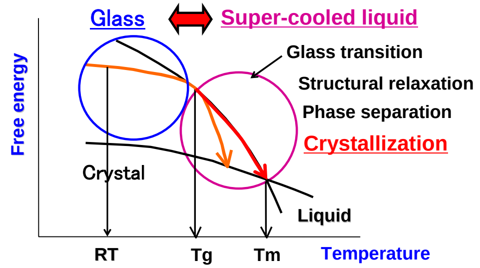
No second-order optical nonlinearity
No ferroelectric properties

↓

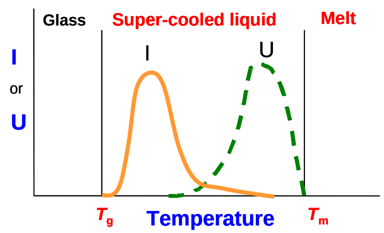
Not active in light control

↓

Glass/Crystal Hybrid Materials



Materials design based on glass crystallization



I : Nucleation rate
U: Crystal growth rate

Control

↓

Microstructure design

Crystallization of Glass

Glass

↓

Nanocrystals

↓

Oriented ceramics

↓

Single crystals

Glass/Crystal Hybrid Materials

↓

Devices

Transparent nanocrystallized glass

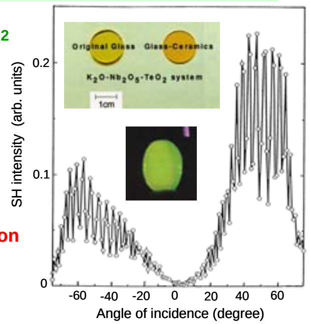
$15K_2O.15Nb_2O_5.70TeO_2$

Nanocrystals (~20nm)

$K[Nb_{1/3}Te_{2/3}]_2O_{4.8}$

Distorted fluorite-type

Light wave conversion
SHG

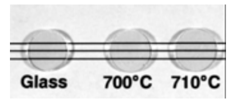


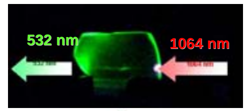
Highly oriented crystallized glass

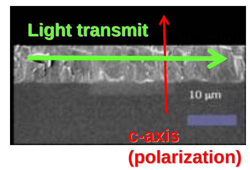
BaO-TiO_2-GeO_2 glasses

$Ba_2TiGe_2O_8$ crystal

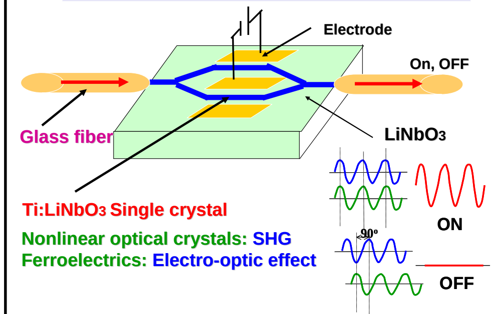
d:~20 pm/V



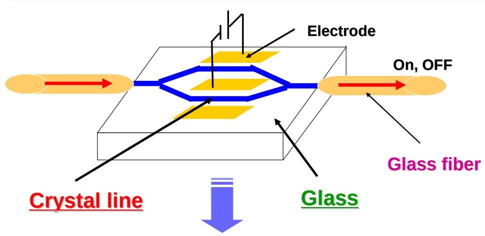




Tunable Optical Switch

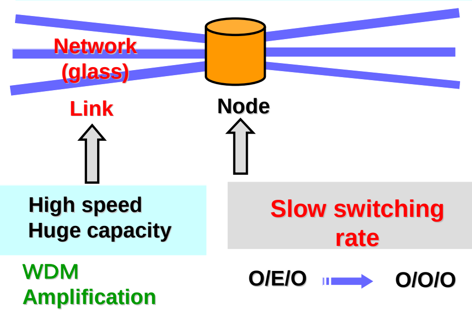


New Tunable Optical Switch using Glass



We need a technique available for spatially selected crystallization of glass

Telecommunication network system



Laser-induced micro-fabrication in glass

1) Hill et al. (1978): Ge-dope SiO_2 fiber + λ=488nm
Refractive index change

2) Osterberg et al. (1986): Ge-dope SiO_2 fiber + λ=1064nm
Second harmonic generation (SHG)

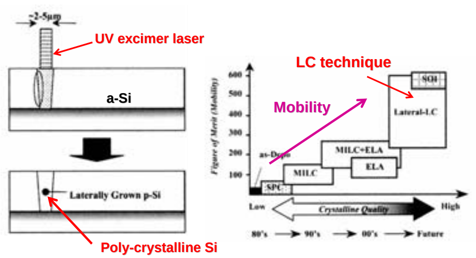
New challenge
in glass science and technology

Glass: SiO_2, Photosensitive glass
Laser: Excimer, Femtosecond
Phenomenon: Refractive index change, hole
Local anisotropy

Patterning and Designing of Crystallization ?

Laser crystallization (LC) in a-Si Engineering

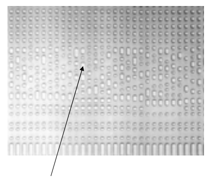
High-quality poly-Si TFT



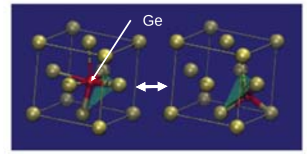
Ref. A.T.Voutsas, Appl. Sur. Sci. 208-209 (2003) 250.

Chalcogenide glasses: DVD $Ge_2Sb_2Te_5$

LD laser: amorphous-crystal transformation (nano-pulse)



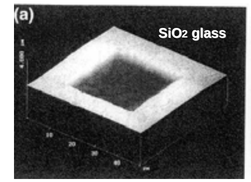
amorphous

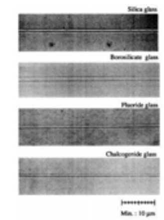


crystal amorphous

A.V.Kolobov et al.
Nature Mater. 3 (2004) 703

Laser Irradiation in Glass





KrF excimer laser: λ=248 nm
K.Sugioka, Ceramics 38(2003)880.

Femtosecond pulsed laser: λ=800 nm
K.Miura et al. Appl. Phys. Lett., 71(1997)3329.

Refractive index change, Abration, Crack,

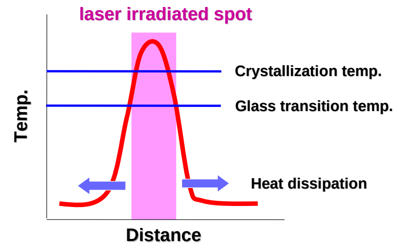
Crystal growth rate *Umax* in oxide glasses

V.M.Fokin et al., J. Non-Cryst. Solids 351 (2005) 789.

$Li_2O.2SiO_2$	70 μm/s
$Na_2O.2SiO_2$	1 μm/s
$CaO.MgO.2SiO_2$ (Diopside)	230 μm/s
$2MgO.2Al_2O_3.5SiO_2$ (Cordierite)	9 μm/s
$2BaO.TiO_2.2SiO_2$ (Fresnoite)	430 μm/s

~1 μs for ~ 1nm growth

CW YAG laser → crystallization



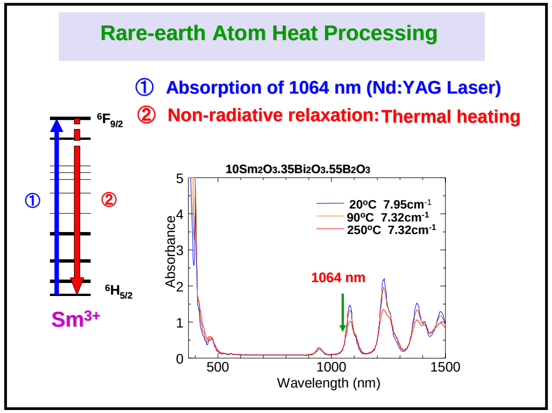
Nano-pulse YAG laser → no crystallization
Lattice vibration (~10^{13}/s) : ~femtosecond
→ Heat dissipation

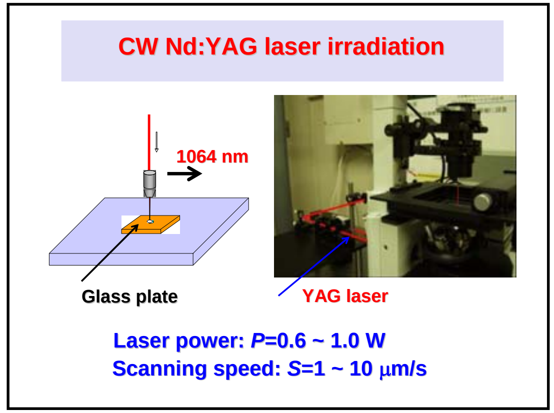
R.Sato, Y.Benino, T.Fujiwara, T.Komatsu,
J. Non-Cryst. Solids 289 (2001) 228.

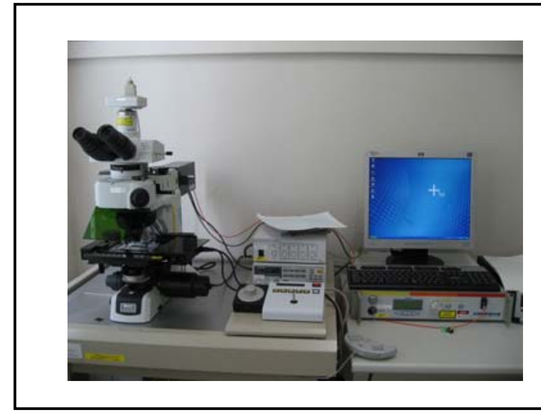
$BaO-Sm_2O_3-TeO_2$ Glass

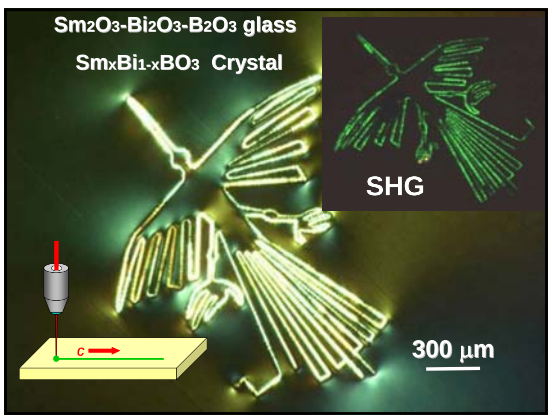
cw Nd:YAG λ=1064 nm

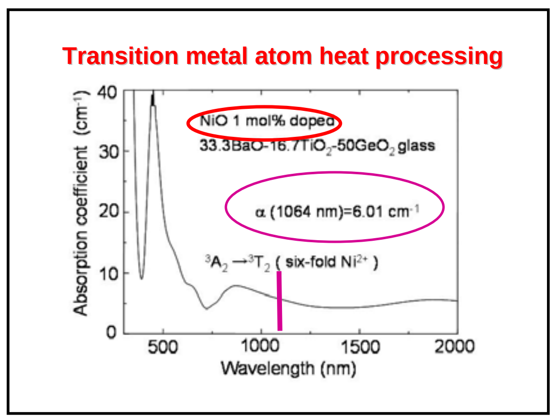
$Sm_2Te_6O_{15}$ crystals

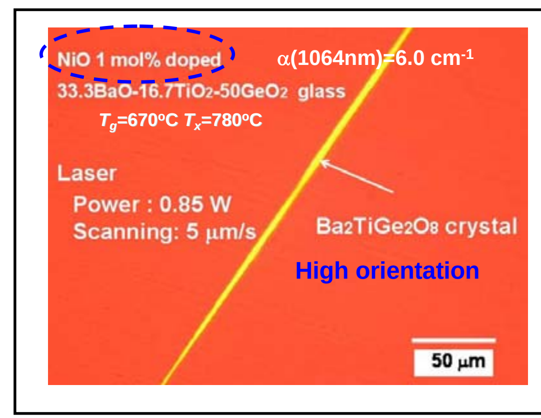

Rare-earth Atom Heat Processing
① Absorption of 1064 nm (Nd:YAG Laser)
② Non-radiative relaxation: Thermal heating
$^6F_{9/2}$
$^6H_{5/2}$
①
②
Sm^{3+}
10Sm2O3.35Bi2O3.55B2O3
20°C 7.95cm-1
90°C 7.32cm-1
250°C 7.32cm-1
1064 nm
Absorbance
Wavelength (nm)

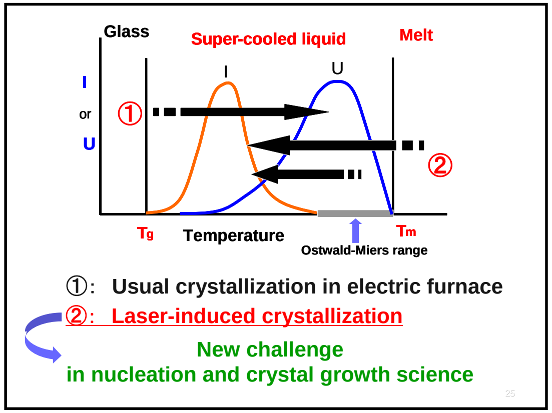

CW Nd:YAG laser irradiation
1064 nm
Glass plate
YAG laser
Laser power: P=0.6 ~ 1.0 W
Scanning speed: S=1 ~ 10 μm/s

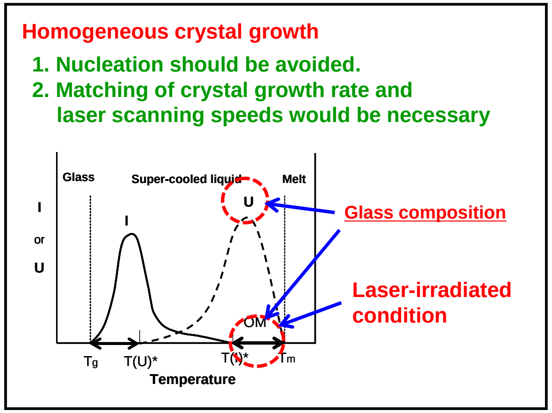


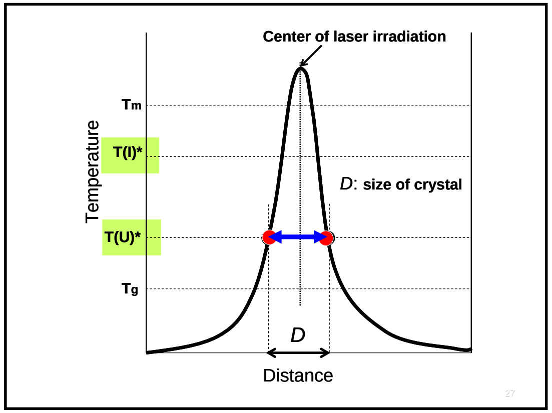

Sm2O3-Bi2O3-B2O3 glass
SmxBi1-xBO3 Crystal
SHG
c
300 μm

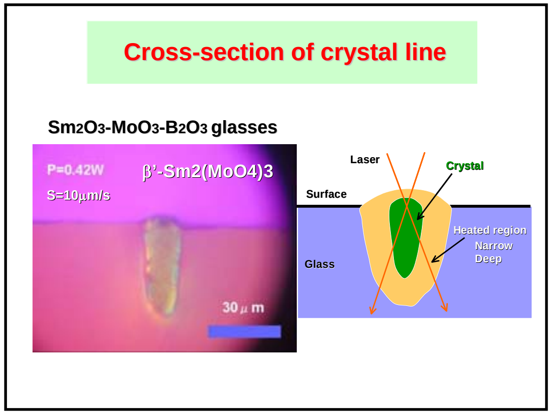

Transition metal atom heat processing
NiO 1 mol% doped
33.3BaO-16.7TiO2-50GeO2 glass
α (1064 nm)=6.01 cm-1
$^3A_2 \rightarrow {}^3T_2$ (six-fold Ni^{2+})
Absorption coefficient (cm-1)
Wavelength (nm)

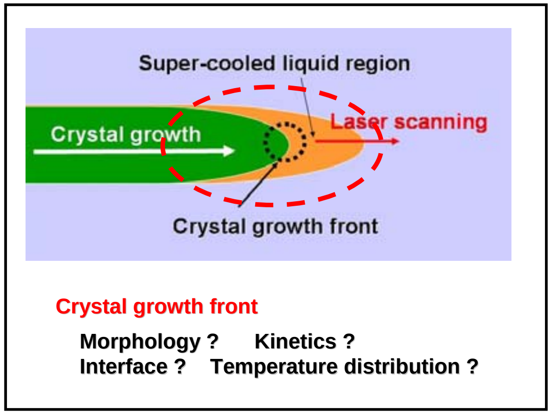

NiO 1 mol% doped
α(1064nm)=6.0 cm-1
33.3BaO-16.7TiO2-50GeO2 glass
T_g=670°C T_x=780°C
Laser
Power : 0.85 W
Scanning: 5 μm/s
Ba2TiGe2O8 crystal
High orientation
50 μm

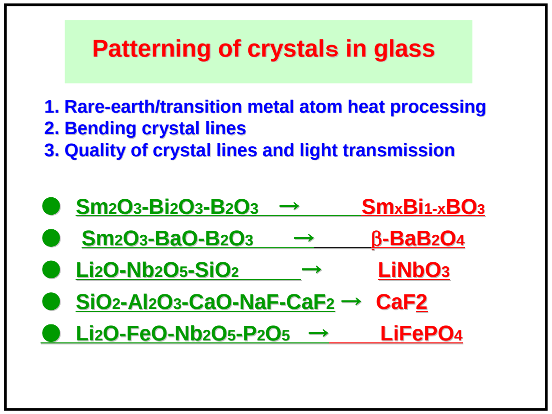

Glass
Super-cooled liquid
Melt
I
or
U
I
U
①
②
Tg
Temperature
Tm
Ostwald-Miers range
①: Usual crystallization in electric furnace
②: Laser-induced crystallization
New challenge
in nucleation and crystal growth science


Homogeneous crystal growth
1. Nucleation should be avoided.
2. Matching of crystal growth rate and
laser scanning speeds would be necessary
Glass
Super-cooled liquid
Melt
I
or
U
U
I
OM
Tg
T(U)*
T(I)*
Tm
Temperature
Glass composition
Laser-irradiated
condition


Center of laser irradiation
Tm
T(I)*
T(U)*
Tg
Temperature
D: size of crystal
D
Distance

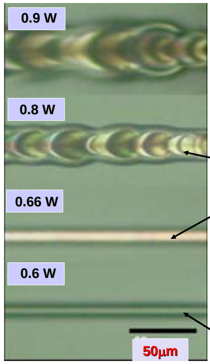

Cross-section of crystal line
Sm_2O_3-MoO_3-B_2O_3 glasses
P=0.42W
S=10μm/s
β'-Sm2(MoO4)3
30μm
Laser
Crystal
Surface
Heated region
Narrow
Deep
Glass


Super-cooled liquid region
Crystal growth
Laser scanning
Crystal growth front
Crystal growth front
Morphology ? Kinetics ?
Interface ? Temperature distribution ?


Patterning of crystals in glass
1. Rare-earth/transition metal atom heat processing
2. Bending crystal lines
3. Quality of crystal lines and light transmission
Sm_2O_3-Bi_2O_3-B_2O_3 → $Sm_xBi_{1-x}BO_3$
Sm_2O_3-BaO-B_2O_3 → β-BaB_2O_4
Li_2O-Nb_2O_5-SiO_2 → $LiNbO_3$
SiO_2-Al_2O_3-CaO-NaF-CaF_2 → CaF2
Li_2O-FeO-Nb_2O_5-P_2O_5 → $LiFePO_4$

10Sm$_2$O$_3$.35Bi$_2$O$_3$.55B$_2$O$_3$

T_g=474°C, T_x=574°C

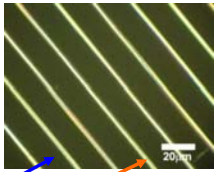


Sm$_x$Bi$_{1-x}$BO$_3$
Crystal
Temp. >> T_x

Temp. < T_x
Refractive index change

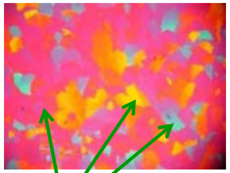
Sm$_2$O$_3$-Bi$_2$O$_3$-B$_2$O$_3$ glass → Sm$_x$Bi$_{1-x}$BO$_3$

YAG laser
Power: 0.66W
Scanning speed: 10μm/s



Glass
Crystal

Electric Furnace
Surface crystallized glass

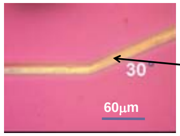


Random orientation

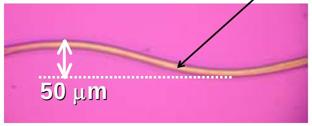
Polarization optical microscopy

Bending / Quality of crystal lines

8Sm2O3.37Bi2O3.55B2O3 glass

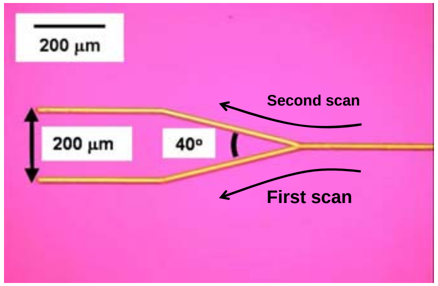


SmxBi1-xBO3
Crystal



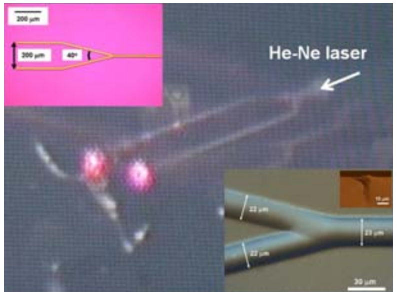
8Sm$_2$O$_3$-37Bi$_2$O$_3$-55B$_2$O$_3$ glass → Sm$_x$Bi$_{1-x}$BO$_3$

P=0.9 W *S*=4 μm/s



Sm$_2$O$_3$-Bi$_2$O$_3$-B$_2$O$_3$ glass → Sm$_x$Bi$_{1-x}$BO$_3$

CW Nd:YAG laser with λ=1064nm
P=0.9W, *S*=5μm/s

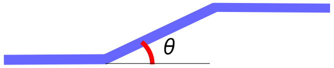


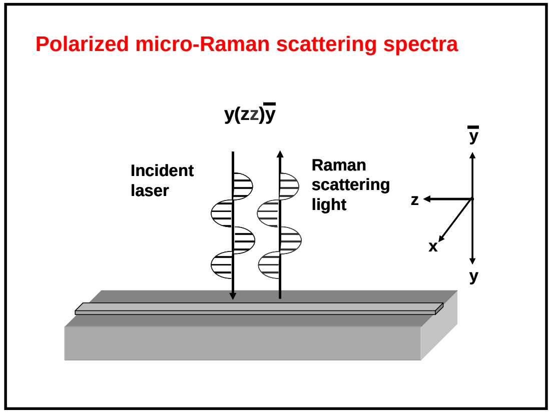
Critical angle for total reflection

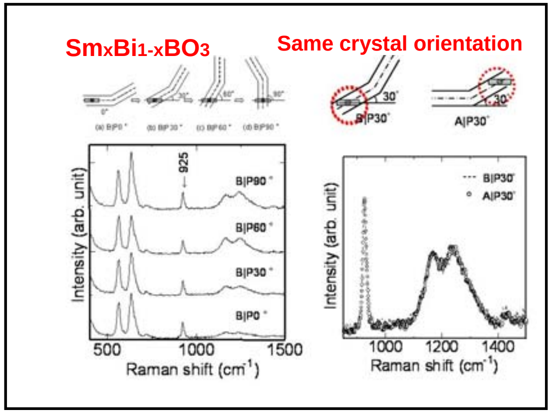
	Glass	Crystal
n	1.964	2.070
Δn (%)	5.43	

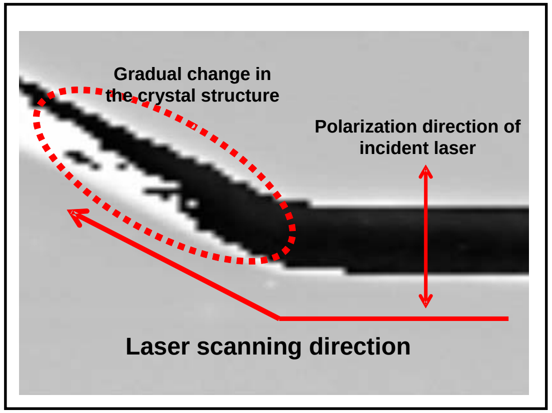
※ λ=632.8 nm

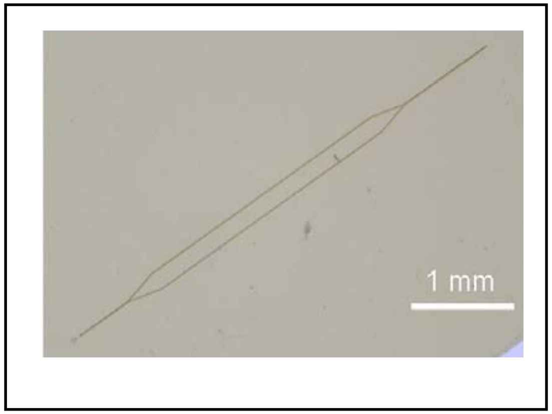
$\theta_{MAX} \fallingdotseq 36^\circ$

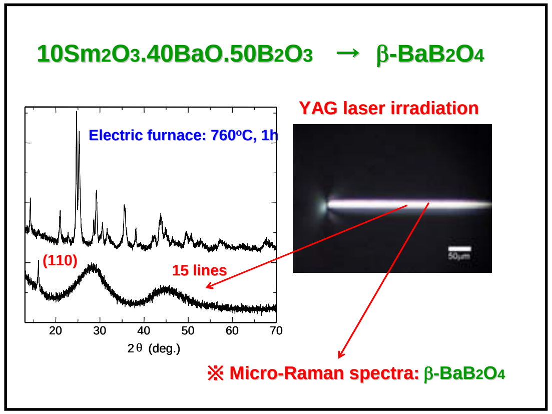


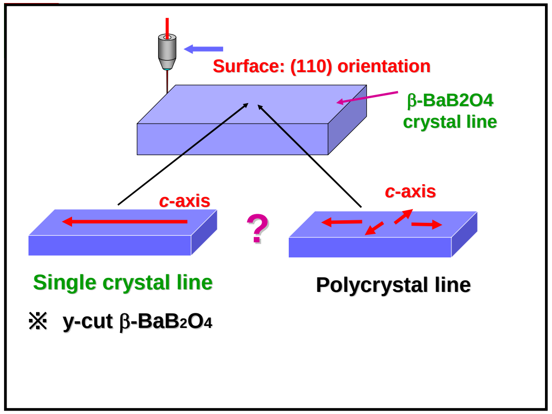

Polarized micro-Raman scattering spectra
y(zz)ȳ
Incident laser
Raman scattering light
ȳ
z
x
y

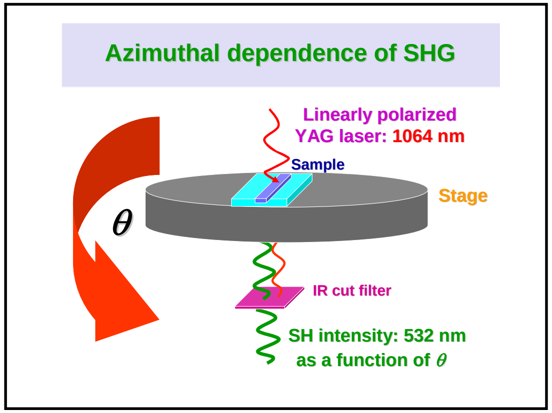

SmxBi1-xBO3
Same crystal orientation
30°
B||P30°
A||P30°
925
B||P90°
B||P60°
B||P30°
B||P0°
Intensity (arb. unit)
500
1000
1500
Raman shift (cm-1)
1000
1200
1400

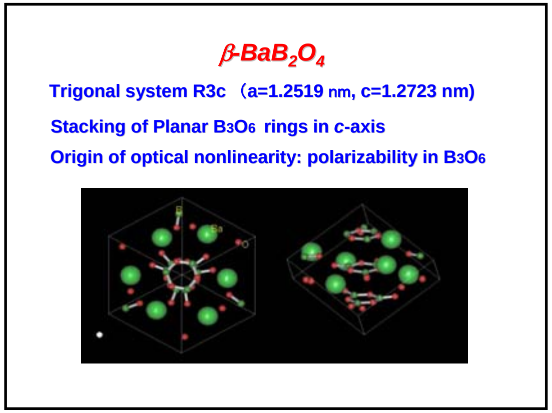

Gradual change in the crystal structure
Polarization direction of incident laser
Laser scanning direction

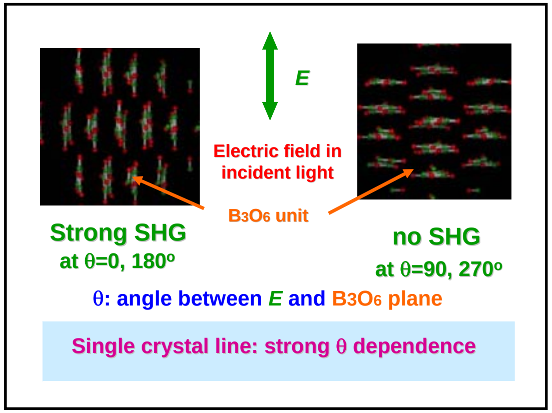

1 mm

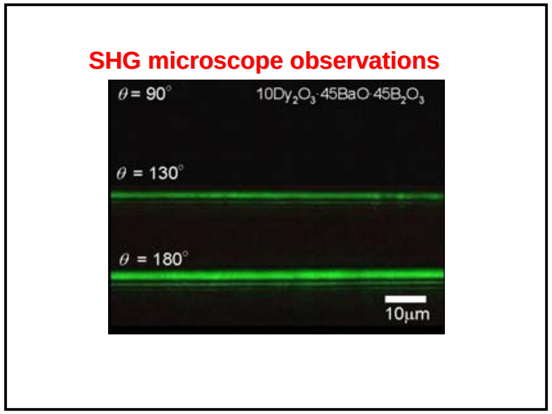

10Sm2O3.40BaO.50B2O3 → β-BaB2O4
YAG laser irradiation
Electric furnace: 760ºC, 1h
(110)
15 lines
20
30
40
50
60
70
2θ (deg.)
※ Micro-Raman spectra: β-BaB2O4

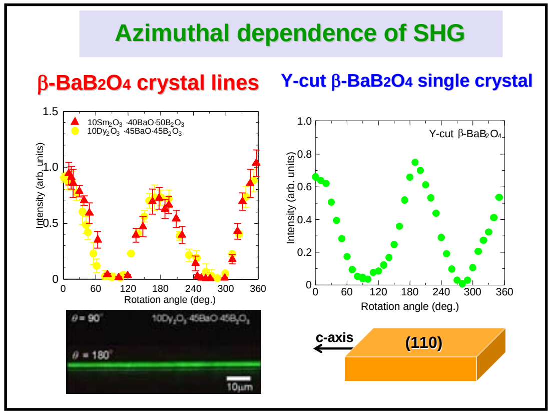

Surface: (110) orientation
β-BaB2O4 crystal line
c-axis
c-axis
?
Single crystal line
Polycrystal line
※ y-cut β-BaB2O4

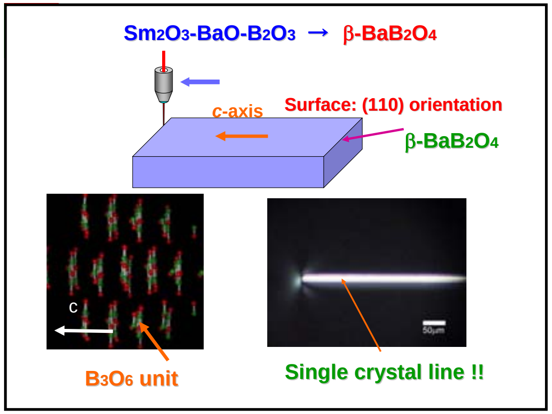

Azimuthal dependence of SHG
Linearly polarized
YAG laser: 1064 nm
Sample
Stage
θ
IR cut filter
SH intensity: 532 nm
as a function of θ


β-BaB2O4
Trigonal system R3c (a=1.2519 nm, c=1.2723 nm)
Stacking of Planar B3O6 rings in c-axis
Origin of optical nonlinearity: polarizability in B3O6


E
Electric field in
incident light
B3O6 unit
Strong SHG
at θ=0, 180º
no SHG
at θ=90, 270º
θ: angle between E and B3O6 plane
Single crystal line: strong θ dependence

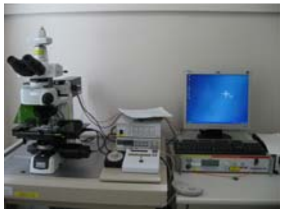

SHG microscope observations
θ = 90°
10Dy2O3·45BaO·45B2O3
θ = 130°
θ = 180°
10μm

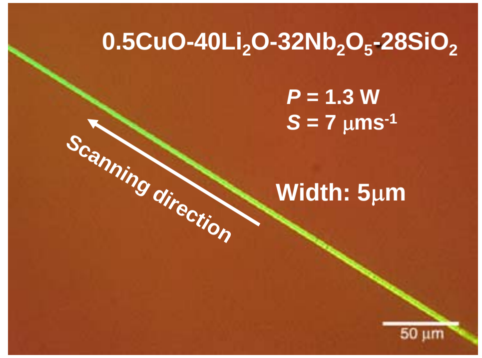

Azimuthal dependence of SHG
β-BaB2O4 crystal lines
Y-cut β-BaB2O4 single crystal
10Sm2O3·40BaO·50B2O3
10Dy2O3·45BaO·45B2O3
Intensity (arb. units)
Rotation angle (deg.)
Y-cut β-BaB2O4
θ = 90°
θ = 180°
10μm
c-axis
(110)


Sm2O3-BaO-B2O3 → β-BaB2O4
c-axis
Surface: (110) orientation
β-BaB2O4
c
B3O6 unit
Single crystal line !!

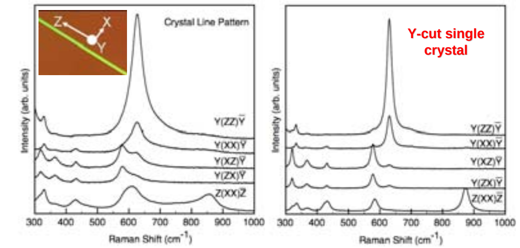
$LiNbO_3$

- Glass
  $0.3wt\%CuO-Li_2O-Nb_2O_5-SiO_2$
- Laser irradiation
  Yb: Fiber laser（λ = 1080 nm）



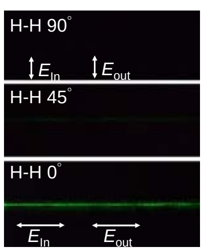


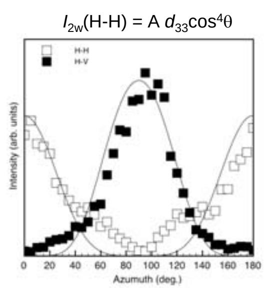
Polarized micro-Raman spectra



High orientation: c-axis growth

SHG from crystal line

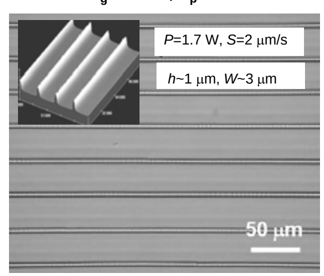


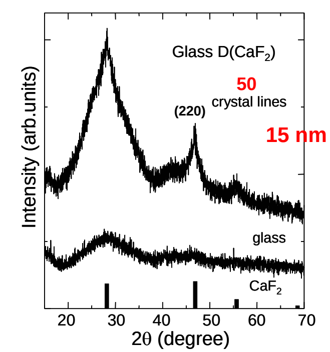


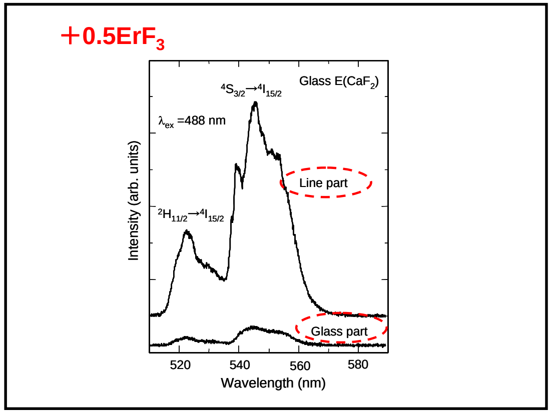
Oxyfluoride glass: fluoride crystal

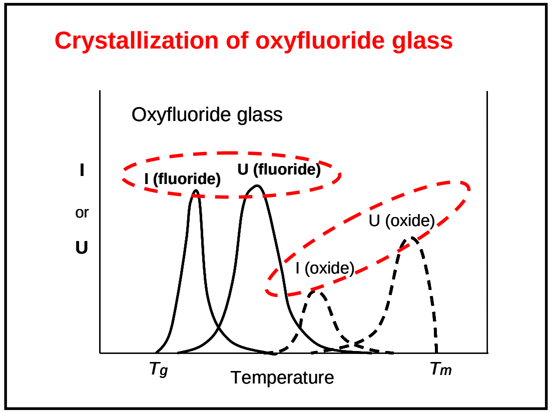
$43SiO_2-22Al_2O_3-5CaO-13NaF-17CaF_2-3NiO$

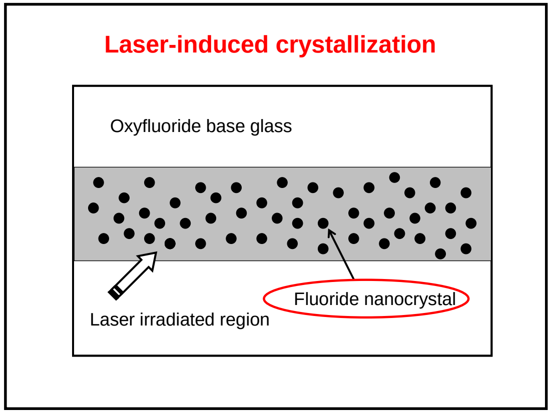
T_g=573°C, T_p=617°C

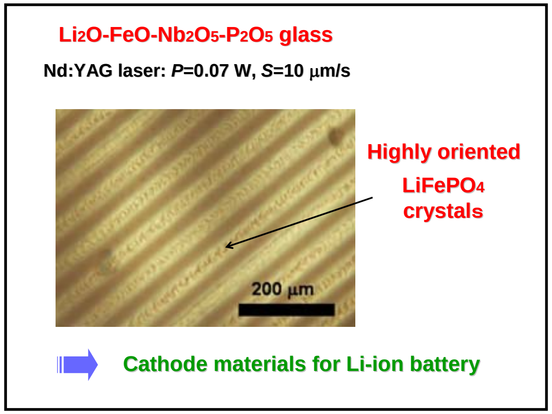


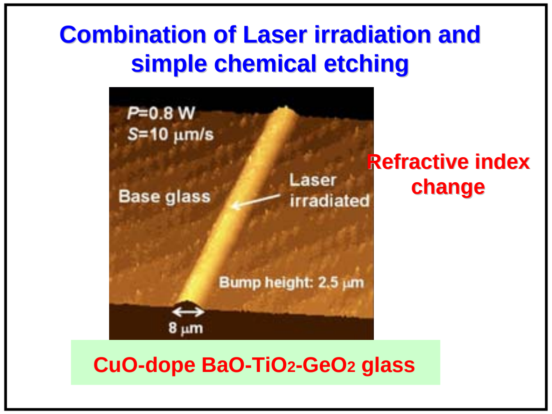


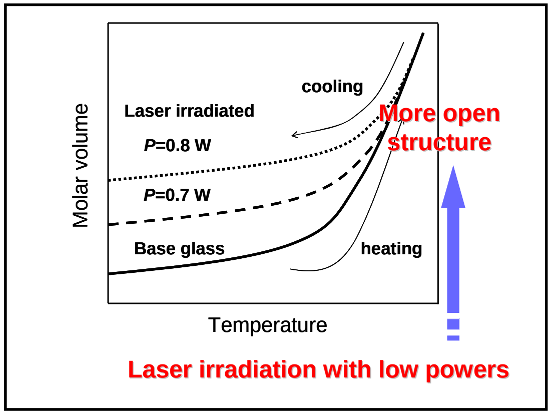

+0.5ErF3
Glass E(CaF2)
4S3/2→4I15/2
λex =488 nm
Line part
2H11/2→4I15/2
Intensity (arb. units)
Glass part
520
540
560
580
Wavelength (nm)


Crystallization of oxyfluoride glass
Oxyfluoride glass
I
or
U
I (fluoride)
U (fluoride)
U (oxide)
I (oxide)
Tg
Temperature
Tm


Laser-induced crystallization
Oxyfluoride base glass
Fluoride nanocrystal
Laser irradiated region

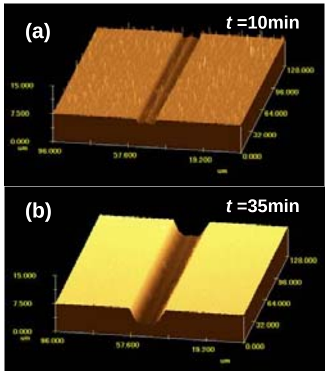

Li2O-FeO-Nb2O5-P2O5 glass
Nd:YAG laser: P=0.07 W, S=10 μm/s
Highly oriented
LiFePO4
crystals
200 μm
Cathode materials for Li-ion battery


Combination of Laser irradiation and
simple chemical etching
P=0.8 W
S=10 μm/s
Base glass
Laser
irradiated
Refractive index
change
Bump height: 2.5 μm
8 μm
CuO-dope BaO-TiO2-GeO2 glass


Molar volume
cooling
Laser irradiated
More open
structure
P=0.8 W
P=0.7 W
Base glass
heating
Temperature
Laser irradiation with low powers

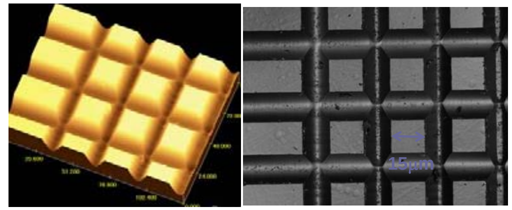
1N HNO_3

U-shape groove



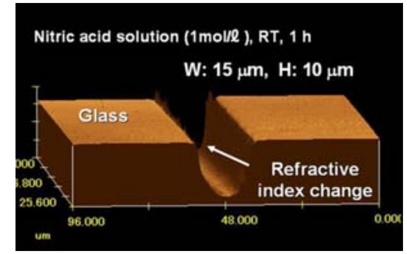
Patterning: P=0.85 W, S=10 μm/s

Etching: 1N HNO_3, 35 min



U-groove depth: 3.5 μm

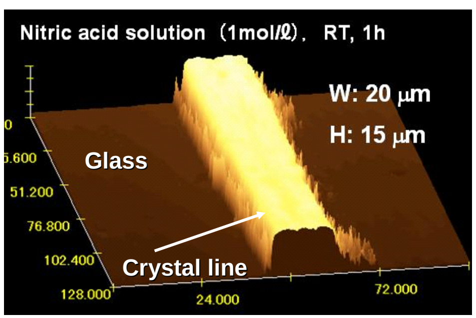
Etching ➡ Crystallization



Etching rate

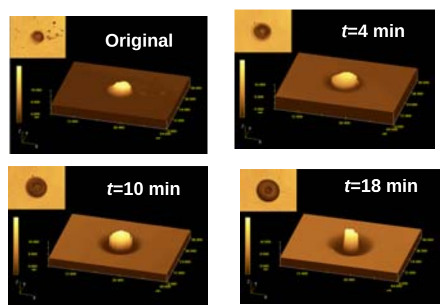
Refractive index > glass > crystal

NiO-doped $BaO-TiO_2-GeO_2$ glass



Etching of crystal dots

P=0.95 W、t=60 s



Summary

Crystallization of glass
+
Laser-induced crystallization

⬇

Design of Glass/Crystal Hybrid Materials

⬇

New micro-devices !!

Laser-induced crystallization

Progress in laser technology

High power laser
Ultra short pulse (femtosecond) laser
Short wavelength laser

※ Conventional technique: everybody can use !

High potential in micro-fabrication

Spatially selected
Direct and non-contact process
Fast and easily automated

Patterning of crystals by laser irradiation

1. Factors

Glass system
glass compositions
Laser irradiation conditions
Laser power
Laser scanning speed

2. Mechanism

Laser-induced nucleation
Very rapid crystal growth: 1 ~ 10 μm/s
→Large temperature gradient in laser irradiated spot (region): large diffusions