Femtosecond laser induced functional microstructures in glass

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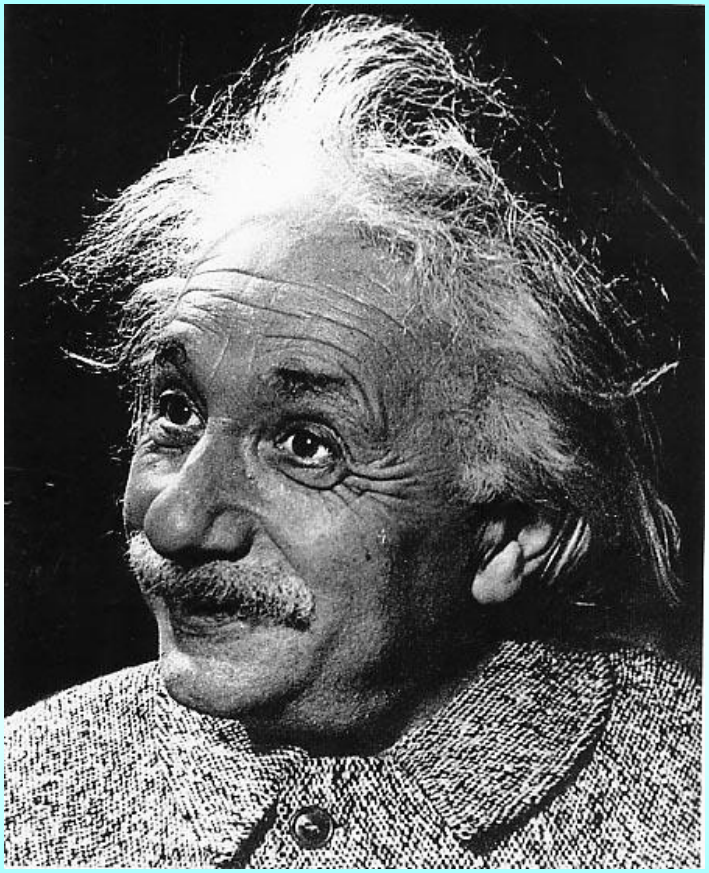
Jan. 11th, 2010

Yuquan, Campus



"Imagination is more important than knowledge"

Albert Einstein

Outline

1、Fs laser and its features

2、Mechanisms about fs laser interaction with matter

3、 Fs laser induced micro-structures in glass and their applications, and fs laser induced phenomena

4、Conclusion

Two greatest theories in the last century
(in the field of science and technology)

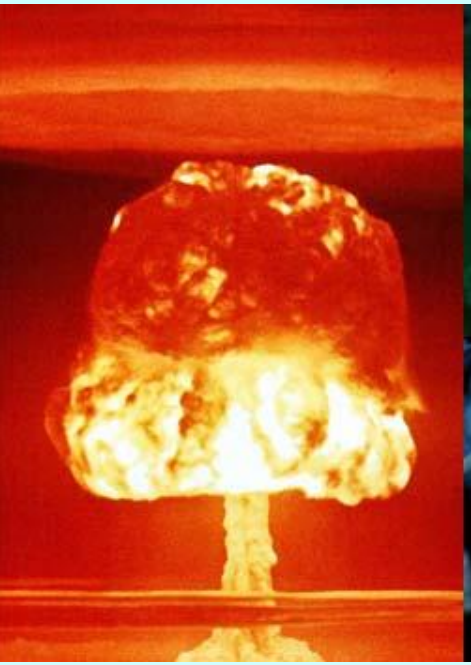
quantum mechanics
量子力学
量子力学

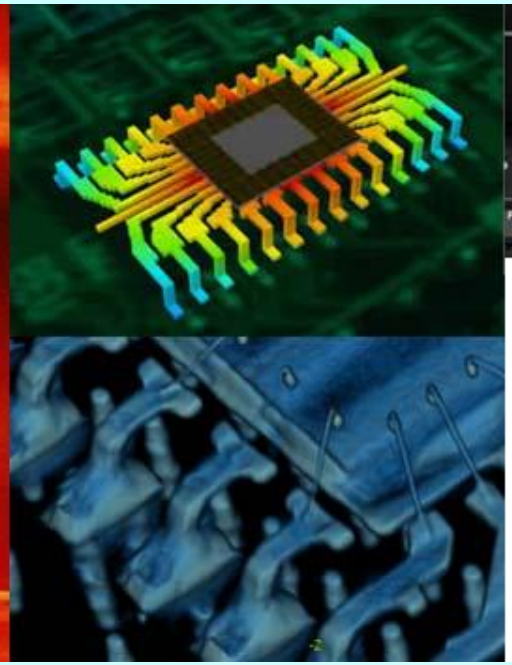
is a set of scientific principles describing the known behavior of energy and matter that predominate at the atomic scale.

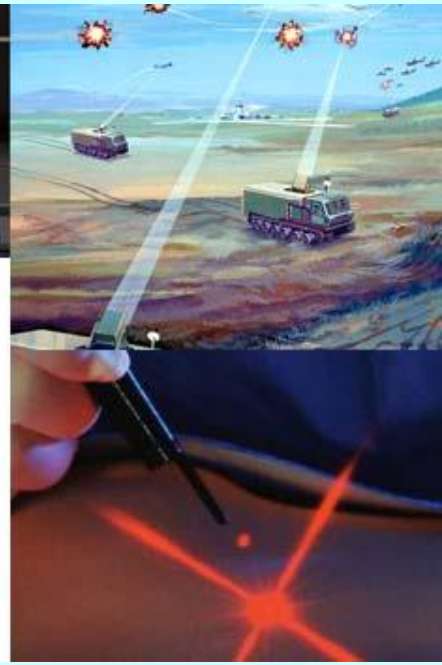
special relativity
狭义相对论
狭義相対論

is a physical theory of measurement in inertial frame of reference

Four greatest inventions in the last century







Atomic energy

Semiconductor

Computer

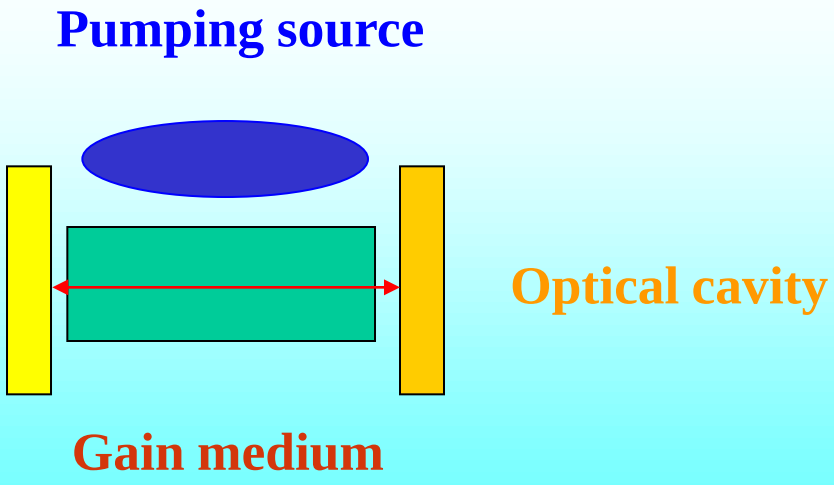
Laser

What is laser?

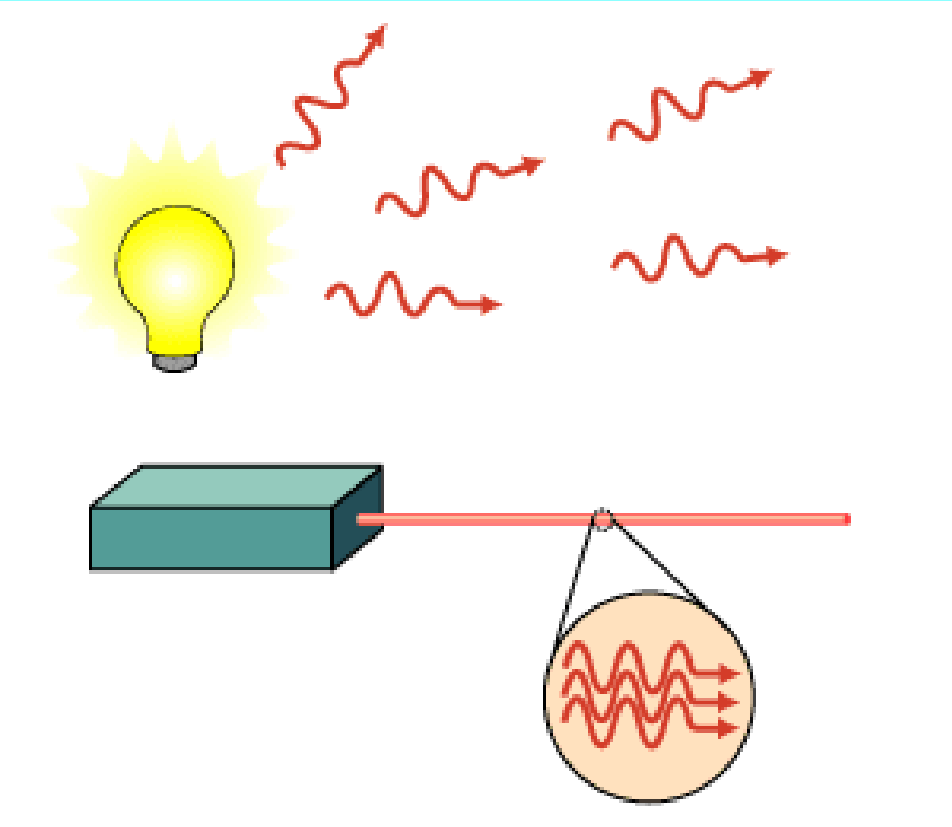
Light amplification by stimulated emission of radiation

激光　雷射(thunder and lightning radiation)

レーザー



Feature of laser



Monochromatic (10^{-10}m) , Narrow beam divergence

High brightness ($4x10^{13}cd/m^2$, $1.7x10^{9}cd/m^2$(sun))

Coherent

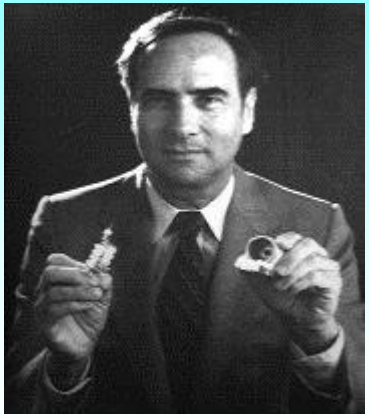
Nobel prize winners for laser

Towens, Prokhorov and Basov

for their works in the field of the maser and the laser

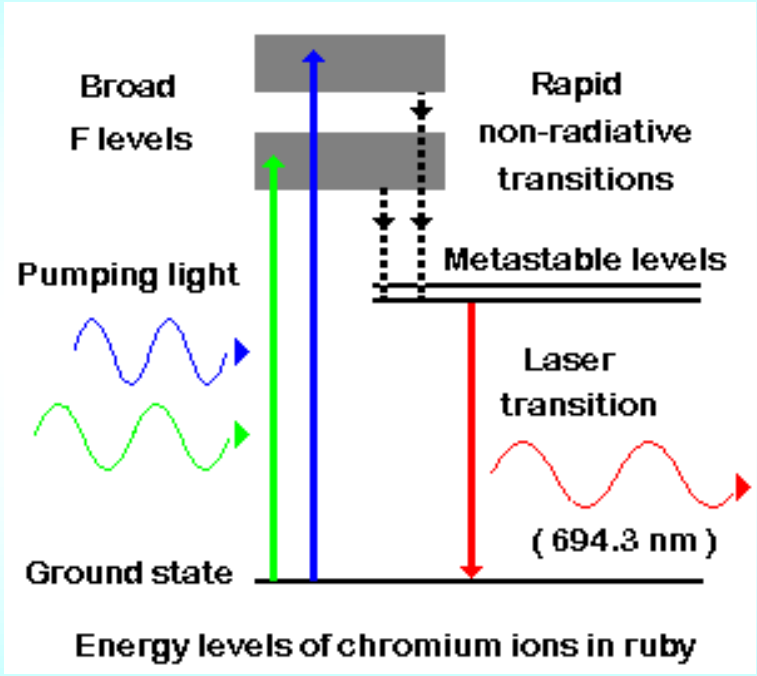
(1964)

First Laser

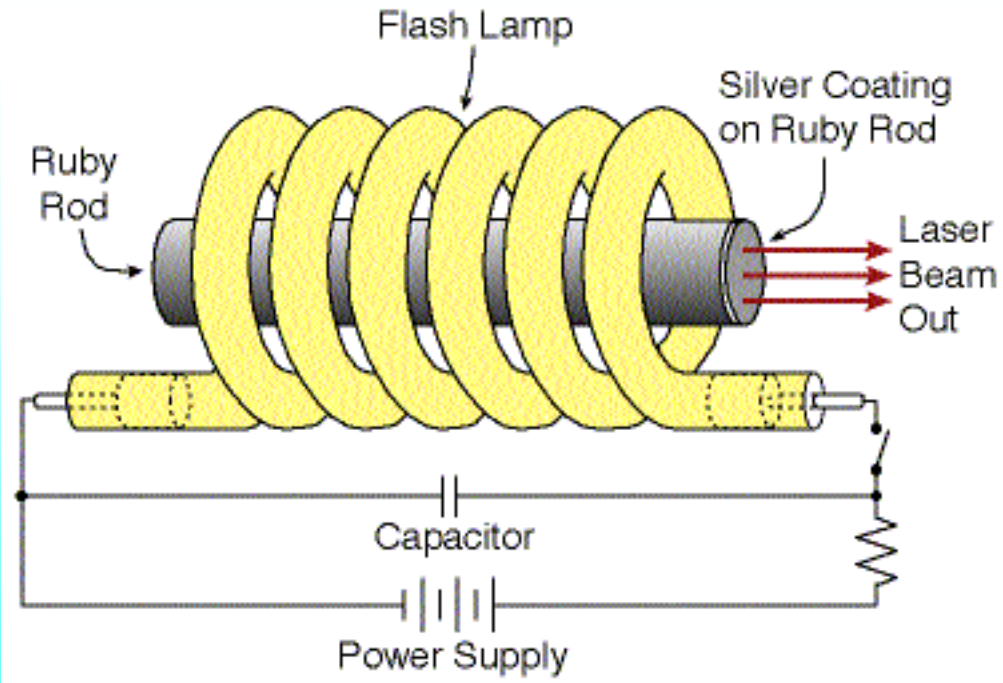


Maiman (1960)

Ruby Laser



Energy levels of chromium ions in ruby



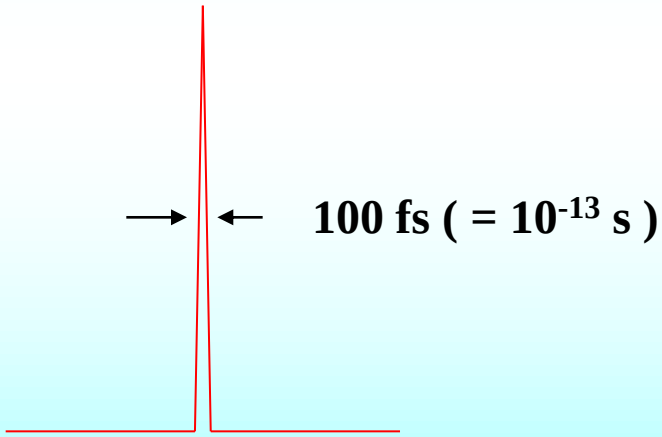
LD

Gas laser（ CO_2, Ar, Excimer ）
Liquid laser (dye)
Solid State laser（ Crystal ，glass ）
Free-electron laser
etc.

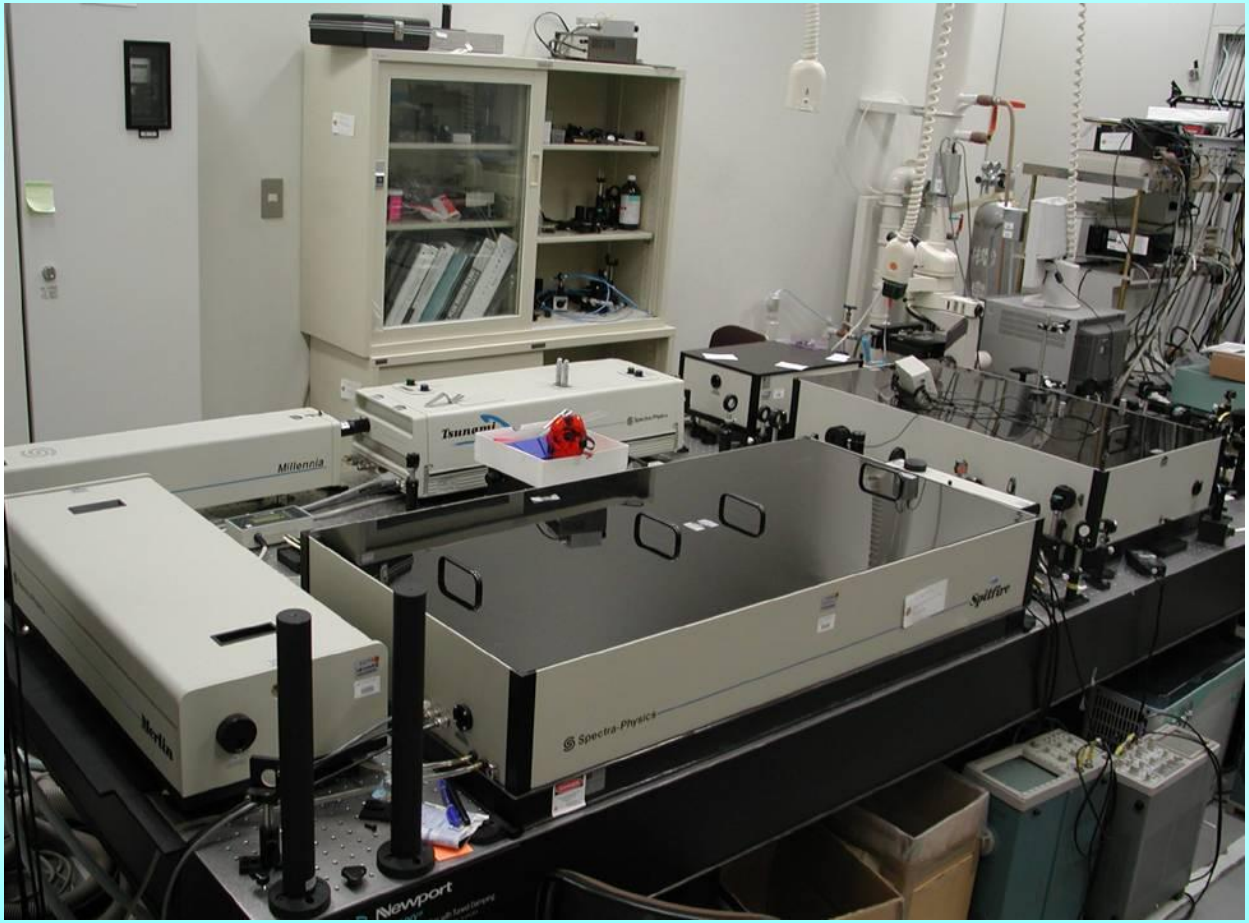
CW laser　　Pulsed laser

What is femtosecond laser?

1fs(飞秒)=10^{-15}s



Femtosecond laser system

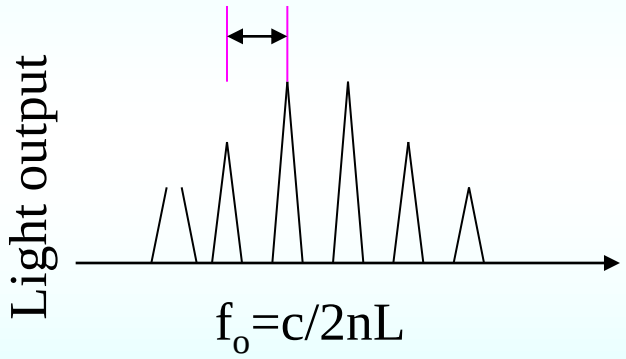


Spectral-physics Co. Ltd

How to realize a femtosecond pulse?

Mode-locking: *Appl. Phys. Lett. 38(1981)671.*

R. L. Fork, B. I. Green and C. V. Shank (Bell Lab.)
CPM (Collision pulse mode-locking) 90fs pulse train

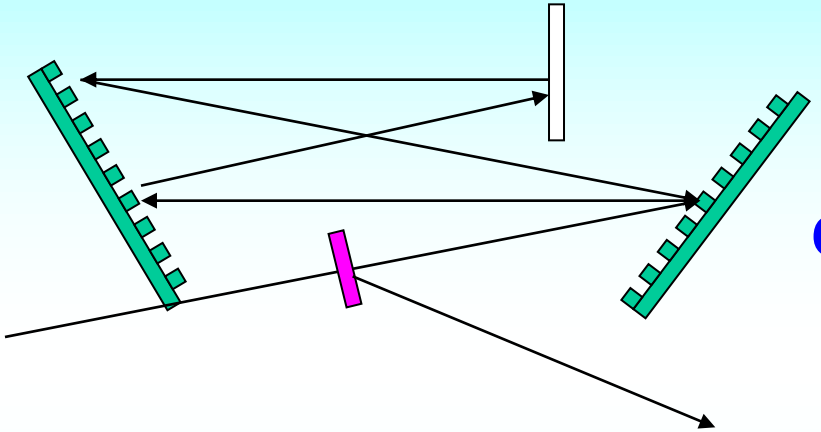


The basis of the technique is to induce a fixed phase relationship between the modes of the laser's resonant cavity. The laser is then said to be *phase-locked* or *mode-locked*. Interference between these modes causes the laser light to be produced as a train of pulses. Depending on the properties of the laser, these pulses may be of extremely brief duration, as short as a few femtoseconds.

How to realize a femtosecond laser pulse with high energy?

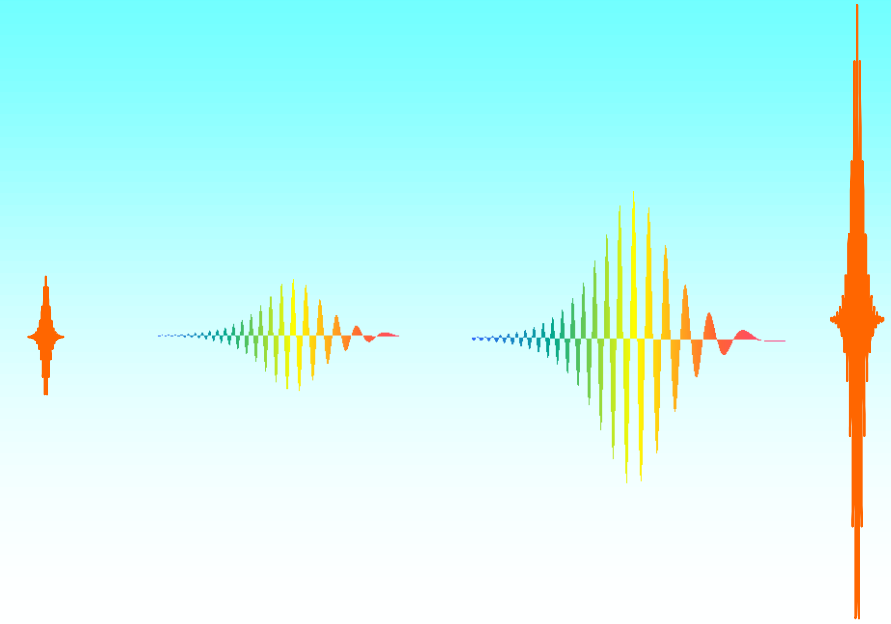
CPA (Chirped pulse amplification): *Opt. Commun. 56(1985)219.*

D. Strickland and G. Mourou (Univ. Rochester)



Chirped mirror

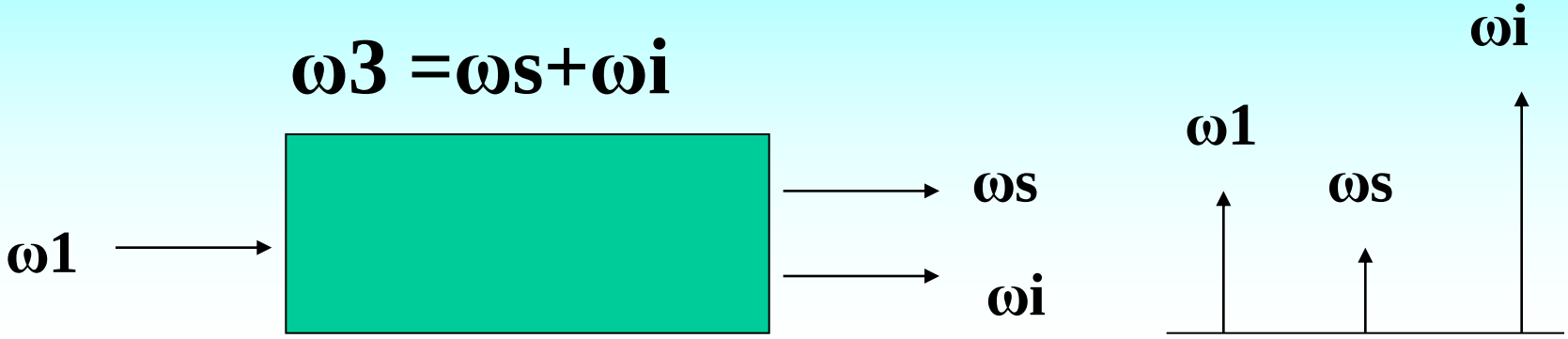
An ultrashort laser pulse is stretched out in time prior to introducing it to the gain medium using a pair of grating that are arranged so that the low-frequency component of the laser pulse travels a shorter path than the high-frequency component does. After going through the grating pair, the laser pulse becomes positively chirped, that is, the high-frequency component lags behind the low-frequency component, and has longer pulse duration than the original by a factor of 103 to 105.



Then the stretched pulse, whose intensity is sufficiently low compared with the intensity limit of gigawatts per square centimeter, is safely introduced to the gain medium and amplified by a factor 106 or more. Finally, the amplified laser pulse is recompressed back to the original pulse width through the reversal process of stretching, achieving orders of magnitude higher peak power than laser systems could generate before the invention of CPA.

How to get a fs laser pulse with various frequency?

Optical parametric oscillation

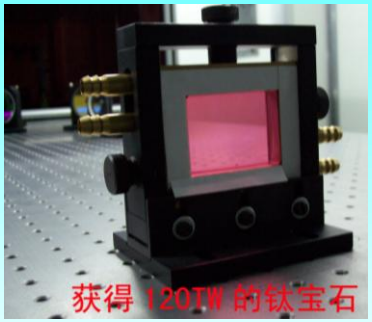


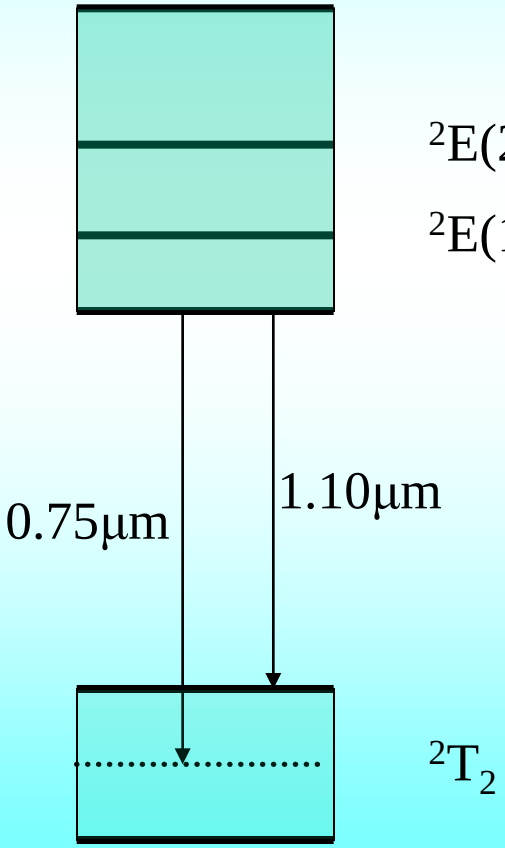
is a parametric osillation which oscillates at optical frequencies. It converts an input laser wave (called "pump") into two output waves of lower frequency (ωs,ωi) by means of nonlinear optical interaction. The sum of the output waves frequencies is equal to the input wave frequency: $\omega s + \omega i = \omega p$. For historic reasons, the two output waves are called "signal" and "idler".

β -BBO(β $-BaB_2O_4$**)**

High $\chi^{(2)}$, mechanical strength, high breakdown threshold

$Ti:Al_2O_3$





1）Large stimulated emission cross-section

2）High hardness，thermal conductivity

3）Available pumping source

4）700nm-1μm tunable

5） easy to be mode-locked

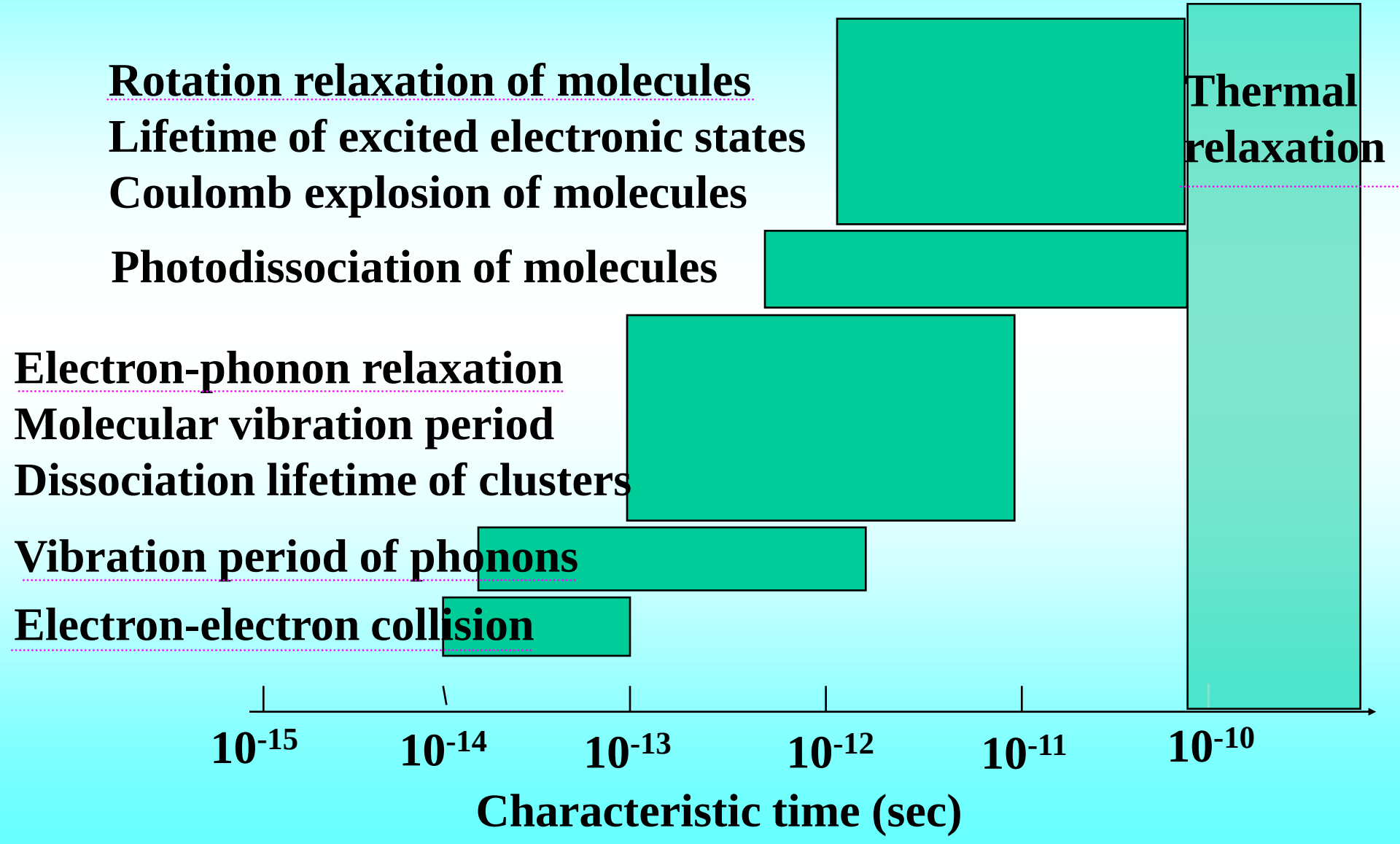
Three features of femtosecond laser:

1) ultrashort pulse

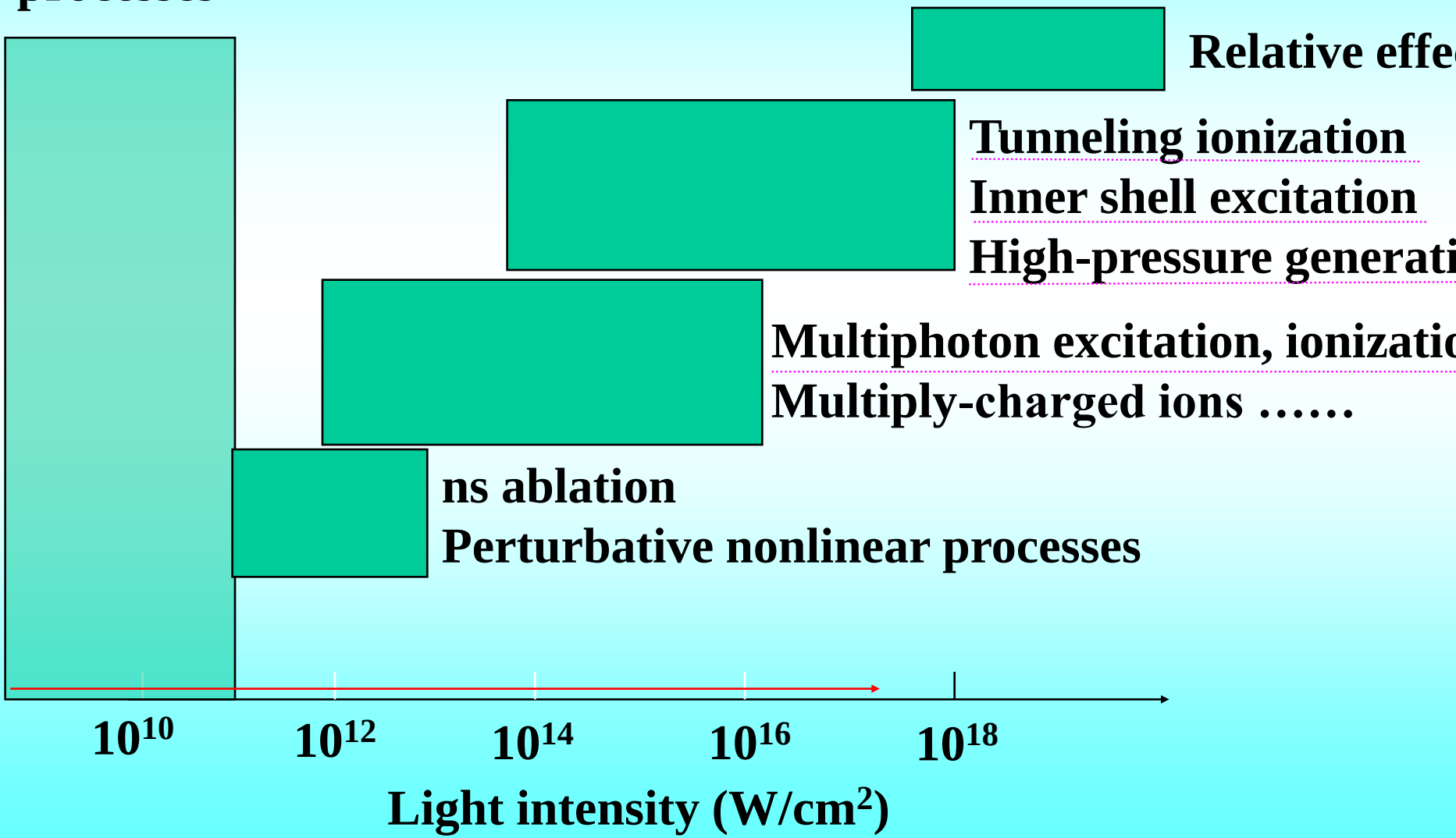
2) ultrahigh light intensity (>2x10^{16}W/cm^{2})

3) ultrabroad bandwidth (coherent) **($\Delta \nu = k / \Delta \tau$)**

Characteristic time of ultrafast processes



Laser-matter interactions



Applications of femtosecond laser

1 Ultrashort pulse

Nonlinear optics

TeraBit optical communication（soliton transmission etc.）

Ultrafast spectroscopy（Pump-Probe spectroscopy）

Multiphoton Microscope

Nano-Bio

Nano-surgery

2 High coherent pulse-train

Multi-photon excitation spectroscopy

Precise measurement of light frequency

3 High electric field

Laser-induced plasma and X-ray

Monochromatic electron beam

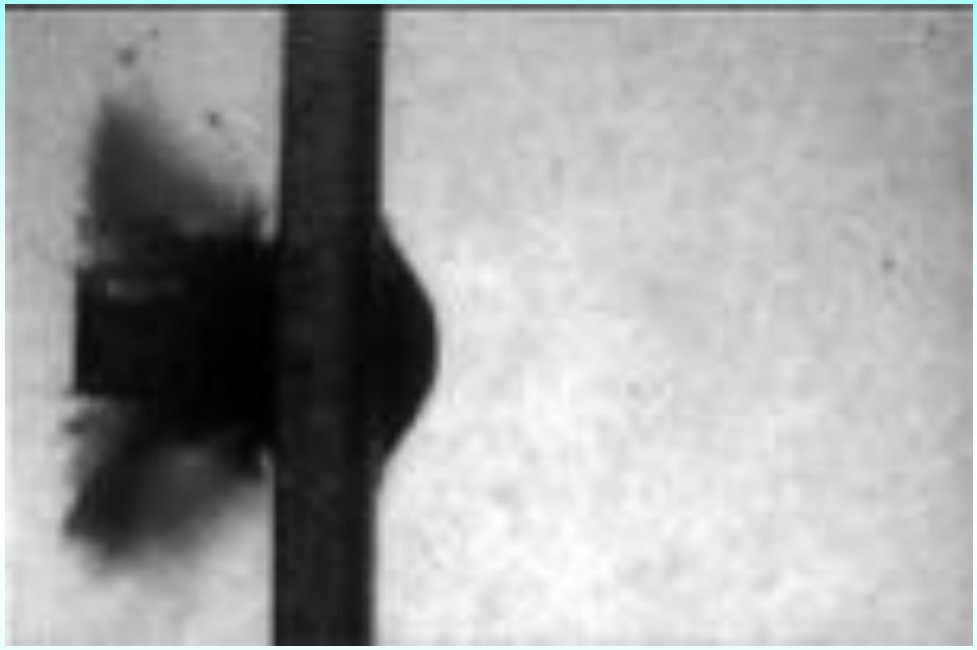
Generation of oriented X-ray and γ-ray

CIF

Laser-triggered lightning

4 High coherent broadband spectrum

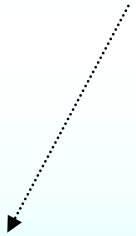
Terahertz time-resolved spectroscopy



Pictures taken during a bullet shooting a steel plate using ultrafast camera
Time resolution: 5μs

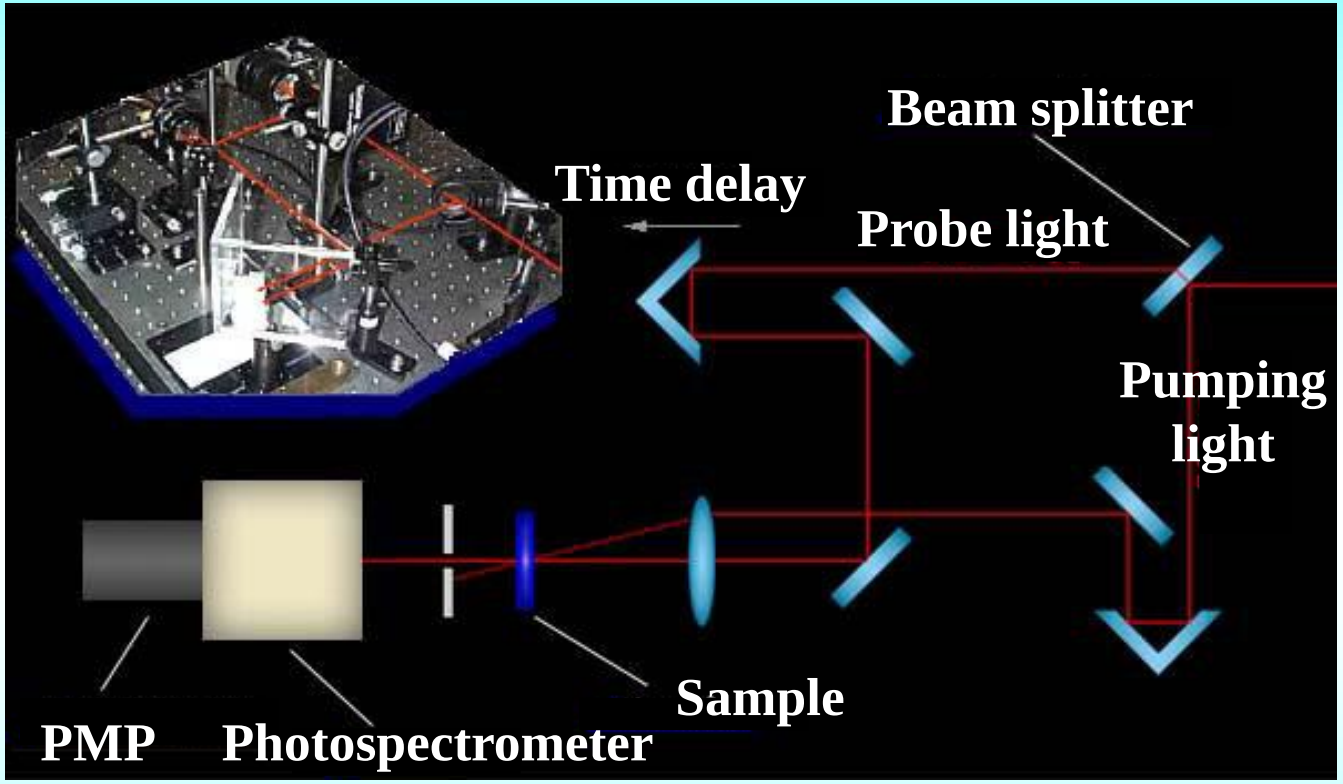
Studying the dynamic process of chemical reaction

$$ICN^{*} \rightarrow [I \cdots CN]^{*} \rightarrow I + CN$$



Intermediate state：life time about 500fs

Femtosecond pump-probe technique

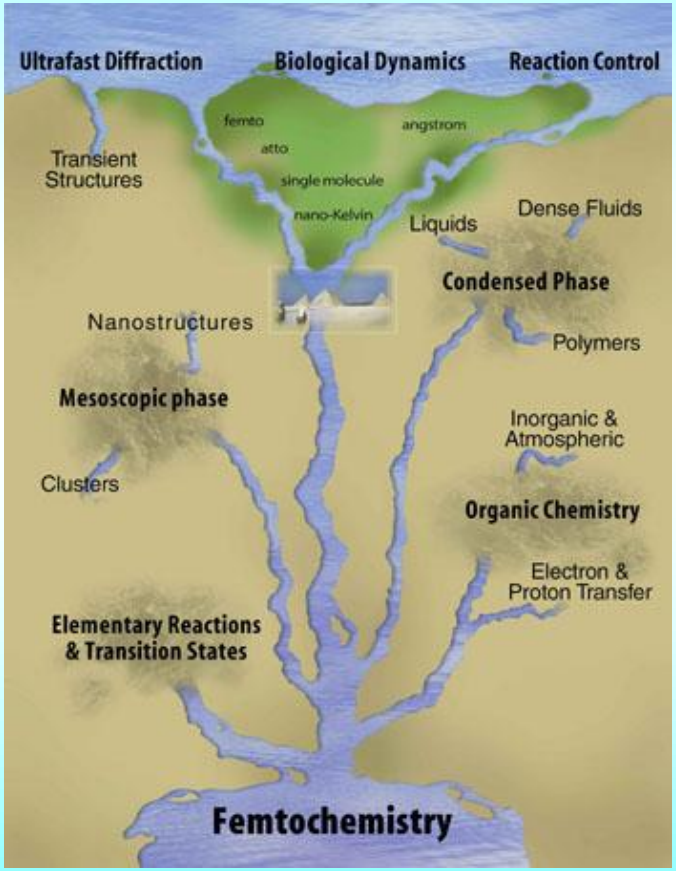


Use two pulses (strong pump and weak probe). A pump pulse excites the sample and triggers the process under investigation. A second delayed pulse, the probe, monitors an optical property. By varying the time delay between the pump and probe pulses, it is possible to assemble measurements as a function of time.

Ultrashort pulse: Femto-spectroscopy

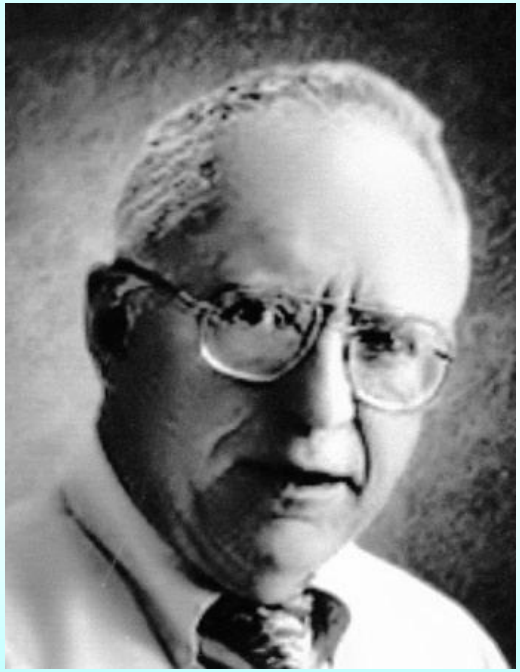
Femtochemistry

Prof. Zewail (Caltech)



for showing that it is possible with rapid laser technique to see how atoms in a molecule move during a chemical reaction.

Ultrashort pulse train: Femto-spectroscopy
Precise measurement of light frequency
(Optical comb)



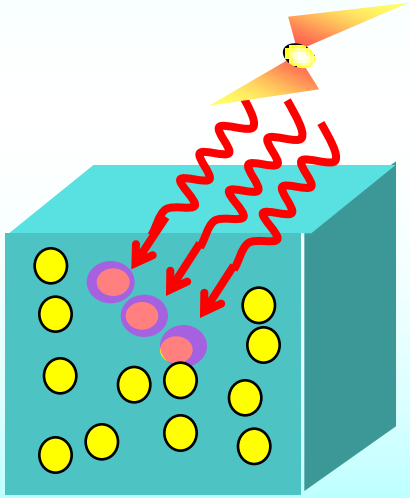
J. L. Hall

T. W. Haensch

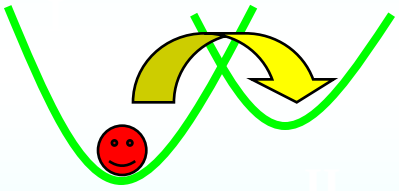
for their contributions to the development of laser-based precision spectroscopy, including the optical frequency comb technique: a very precise tool for measuring different colors—or frequencies—of light, only made possible by recent advances in ultrafast femtosecond lasers.

Basic idea of our research

External field



Glass



- **induced electronic structure**
- **e.g. rare-earth**

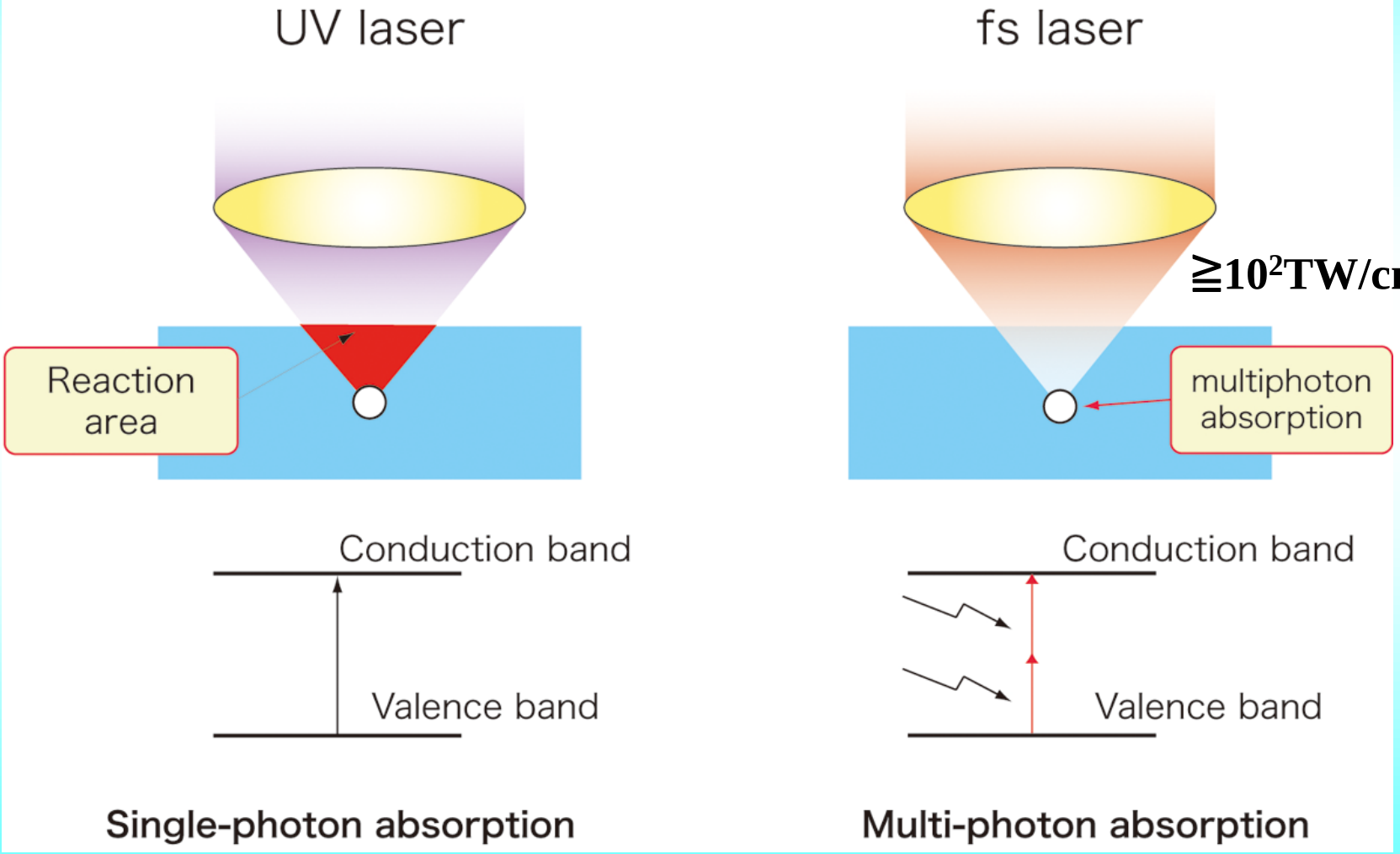
- **Electric field**
- **Magnetic field**
- **Laser**
- **Radiation**
  - .
  - .
  - .

Features of femtosecond laser :

1) Elimination of the thermal effect due to extremely short energy deposition time

2) Participation of various nonlinear processes enabled by high localization of laser photons in both time and spatial domains

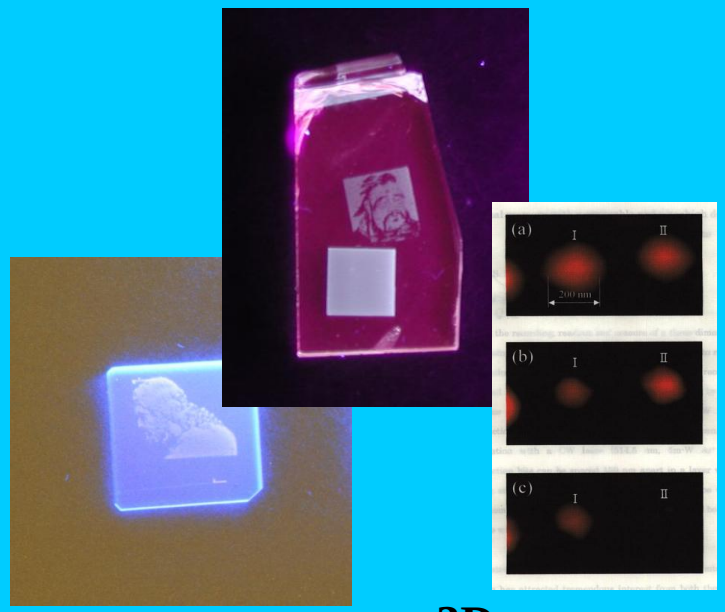
3-dimensional micro-modification



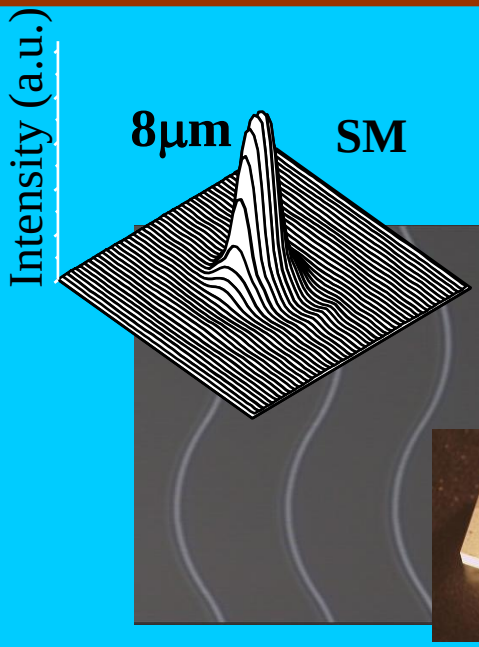
$$\chi = \sigma \left(I/h\nu \right)^{n}$$

Applications of induced microstructures

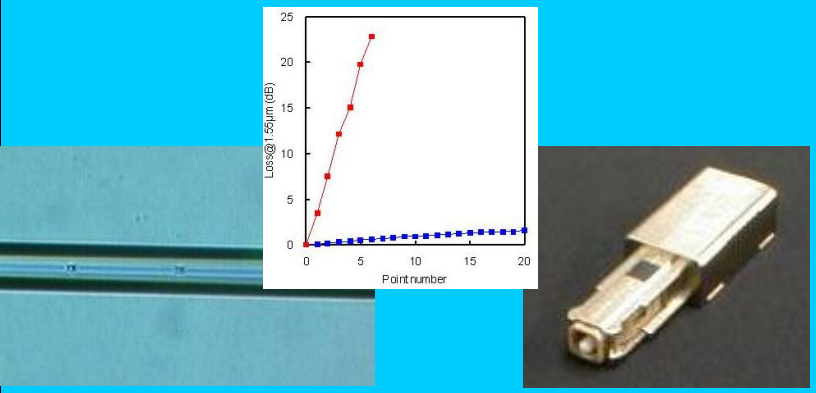
3D image



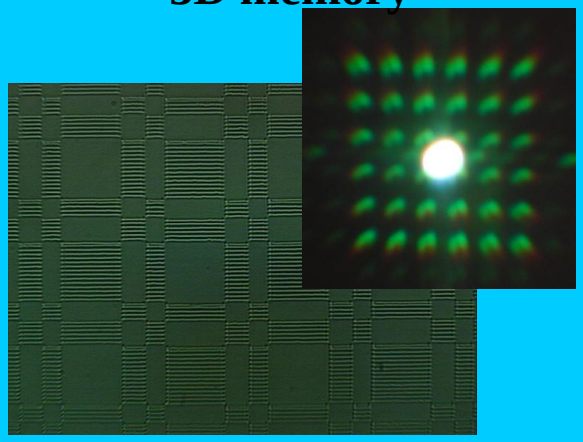
3D memory



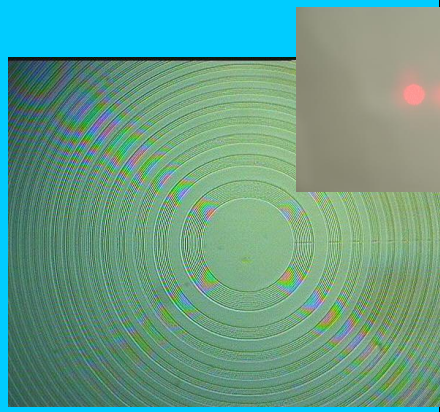
Optical Wavegu



Fiber grating



Micro-grating



Micro-lenz

No intrinsic absorption $n h\omega \geq E_g$

↓

Multiphoton absorption rate $P(I)_{MPI} = \sigma_n I^n$

↓

Avalanche ionization (via impact ionization)

↓

Exponential growth of the free electrons.

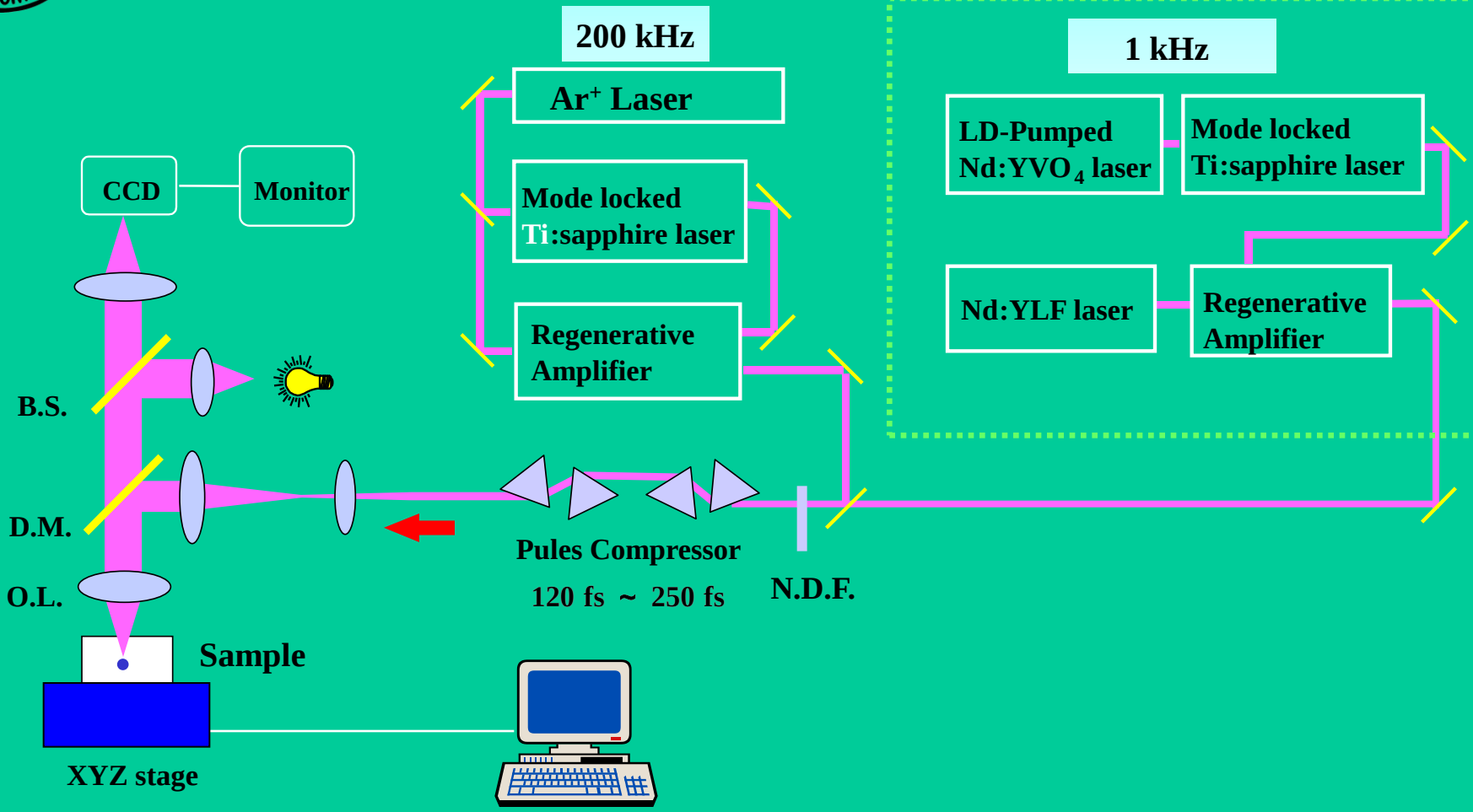
↓

A highly absorptive and dense plasma, induce various phenomena due to nonlinear processes

Some of the related important research

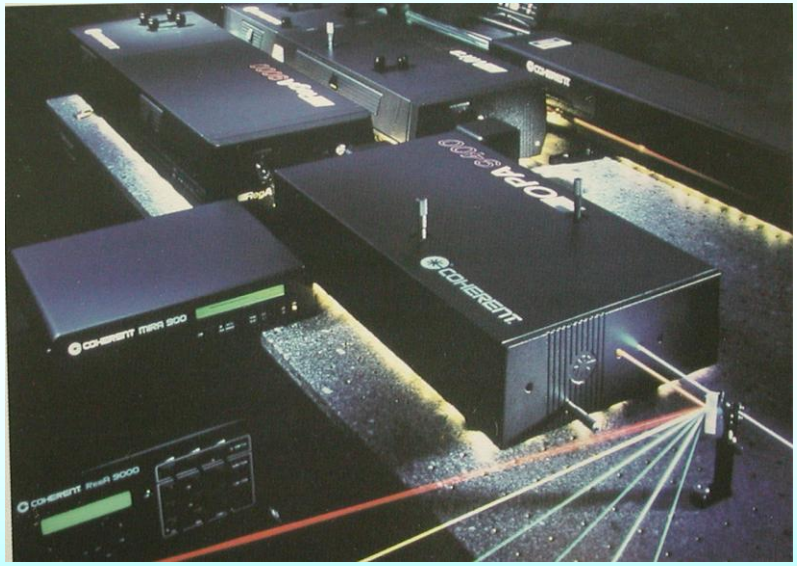
1) H. Misawa, Japanese Patent 1994.
2) K. M. Davis et al., Opt. Lett., 21(1996)1729.
3) E. N. Glezer et al., Opt. Lett., 21(1996)2023.
4) K. Miura et al., Appl. Phys. Lett., 71(1997)3329.
5) S. Juodkazis et al., Phys. Rev. Lett., 96(2006)166101.
6) P. G. Kazansky et al., Phys. Rev. Lett., 82, 2199 (1999).
7) D. Homoelle et al., Opt. Lett., 24(1999)1311.
8) K. Kawamura et al., Appl. Phys. Lett., 79(2001)1228.
9) A. Marcinkevicius et al., Appl. Phys. Lett., 26(2001)277.
10) H. Sun et al., Opt. Lett., 20(2001)325.

Optical setup



Laser systems for direct 3D writing

Pulse energy
5μ J



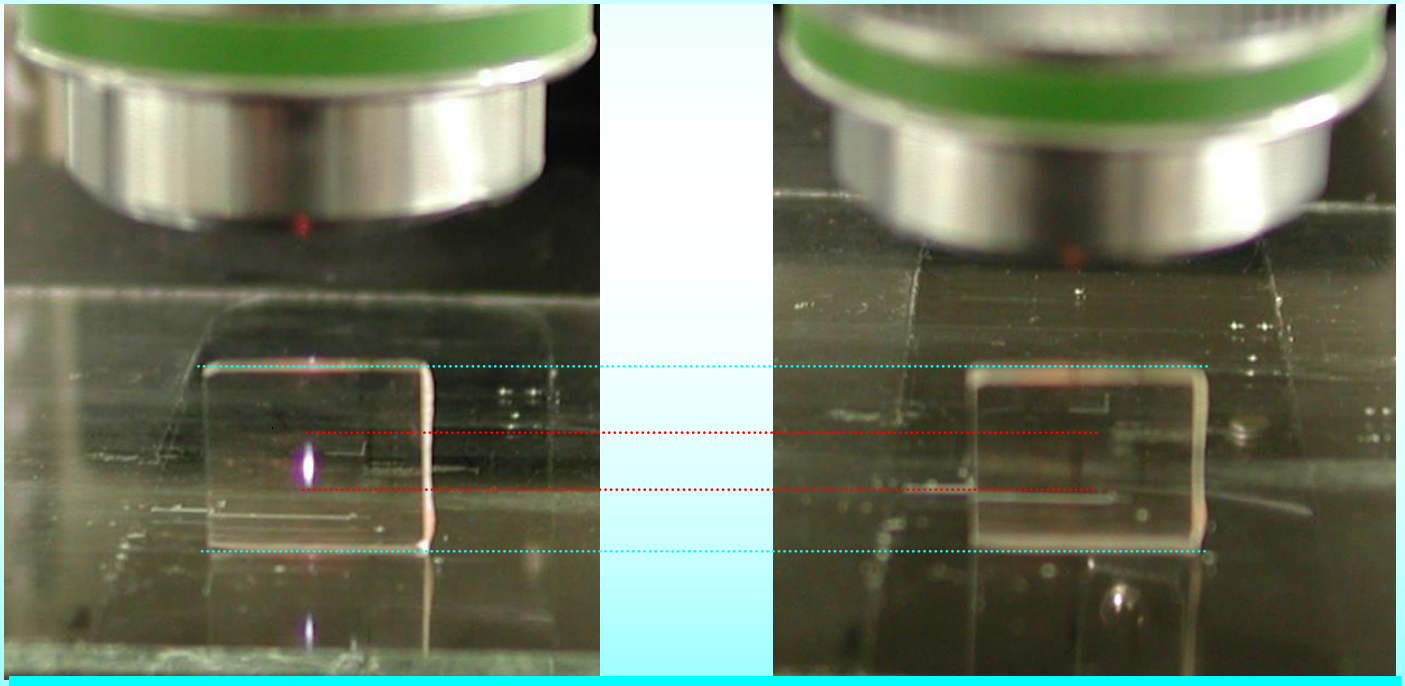
200KHz Ti:Sapphire femtosecond laser system
(Coherent Co. Ltd)

Pulse energy
1m J

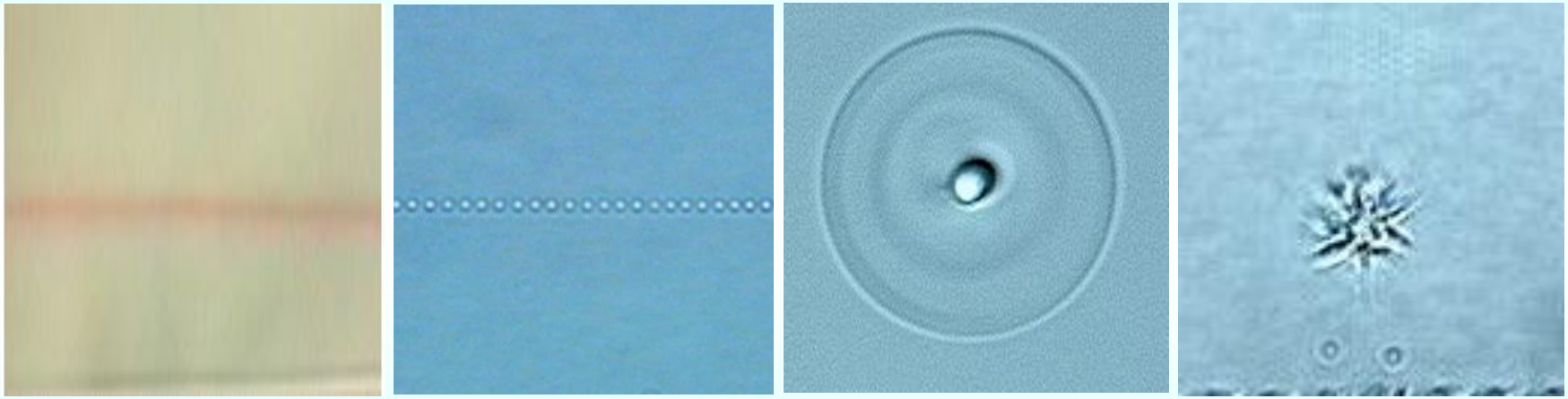
1KHz Ti:Sapphire femtosecond laser system
(Spectra-Physics Co. Ltd)

During and after fs laser irradiation

Emission **Coloration**



Femtosecond laser induced microstructures

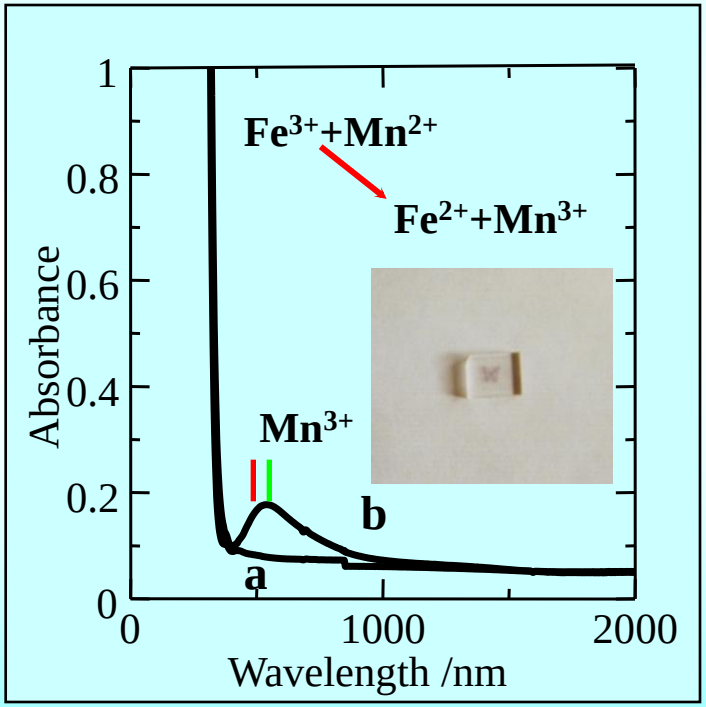


Various structures induced by
800 nm, 120fs laser-pulses

Fs laser induced valence state change of transition metal ions

$$Mn^{2+} + Fe^{3+} + \rightarrow Mn^{3+} + Fe^{2+}$$

1KHz
10x(NA=0.3)
3mW
120fs



$20Na_2O$-$10CaO$-
$70SiO_2$-$0.1Fe_2O_3$-
0.1MnO (mol%)

Absorption spectra
a: before irradiation b: after irradiation (iron and manganese)

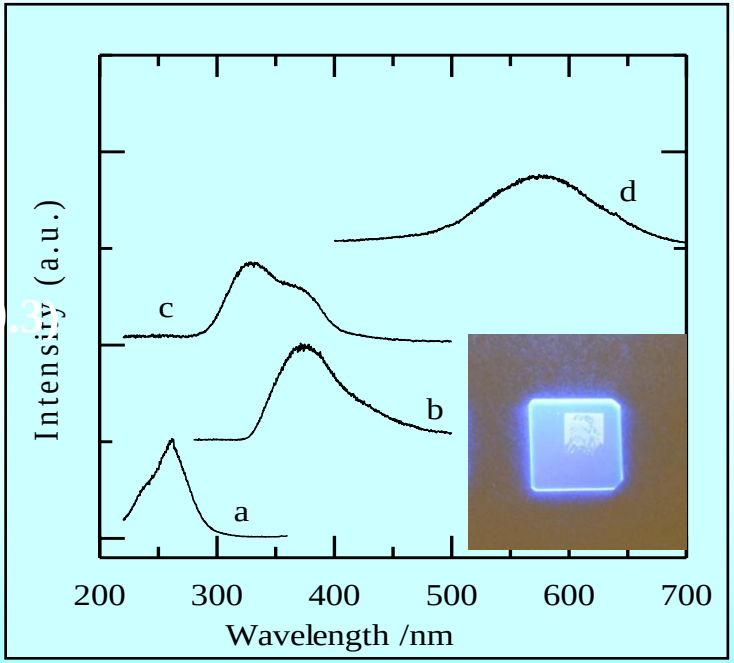
Appl. Phys. Lett., 79(2001)3567.

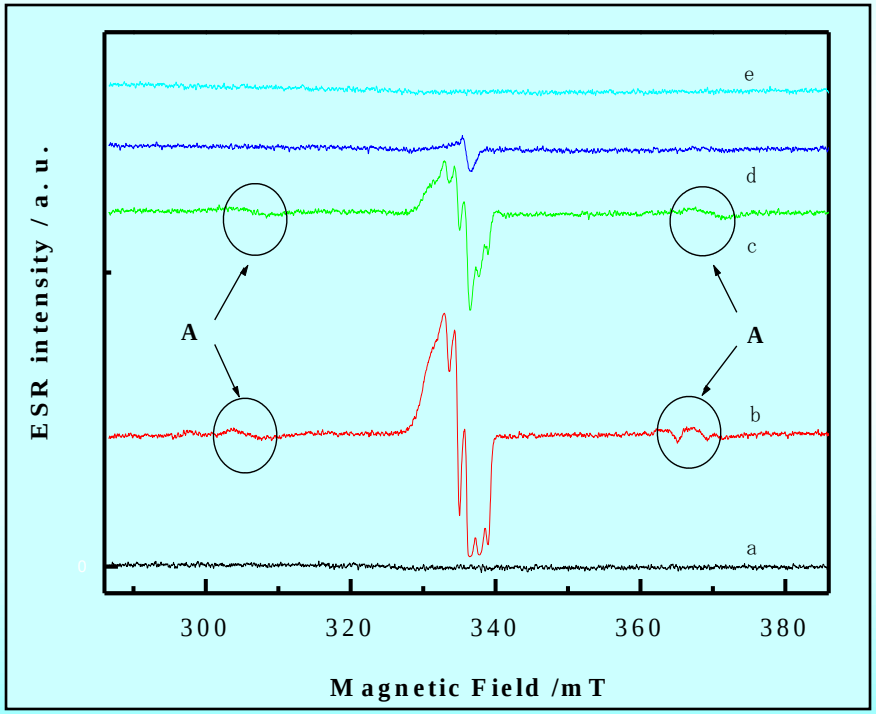
Fs laser induced valence state change of noble metal ions

$$Ag^{+} \rightarrow Ag^{2+} + Ag$$

Opt. Express, 12(2004)4035.

Na_2O-Al_2O_3-P_2O_5-0.1Ag_2O (mol%)





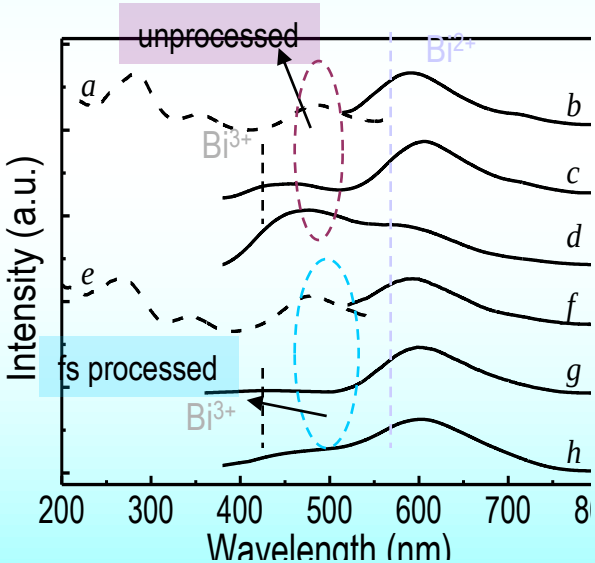
Emission and excitation spectra
a, b: before irradiation
c, d: after irradiation

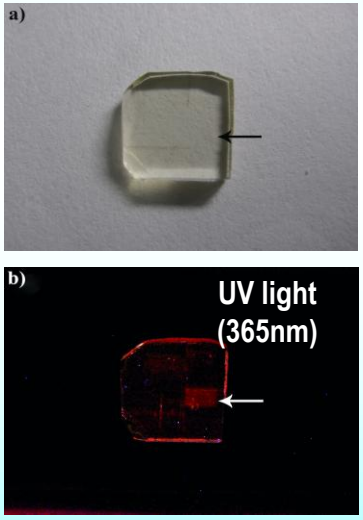
ESR spectra
a: before irradiation b: after irradiation

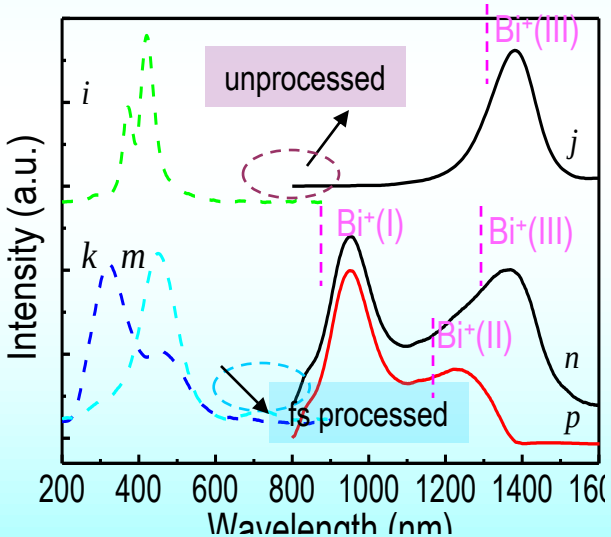
Fs laser induced valence change of heavy metal ions

$Bi^{3+} \rightarrow Bi^{2+} \rightarrow Bi^{+}$

J. Mat. Chem. 19(2009)4603.



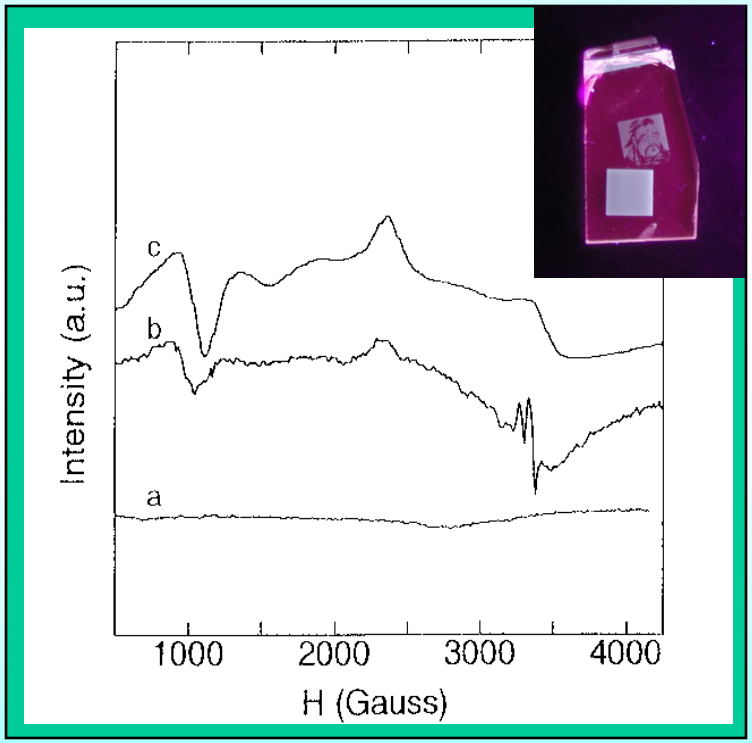




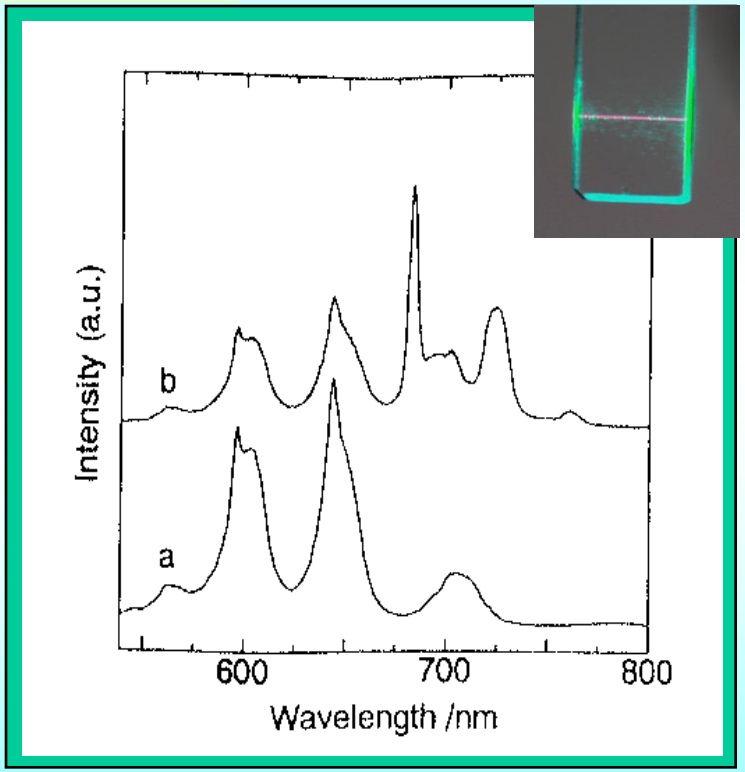
Visible and infrared luminescence changes after fs laser irradiation

Fs laser induced valence change of rare earth ions

$Eu^{3+} \rightarrow Eu^{2+}$ *Appl. Phys. Lett.*, 74(1999)10. $Sm^{3+} \rightarrow Sm^{2+}$

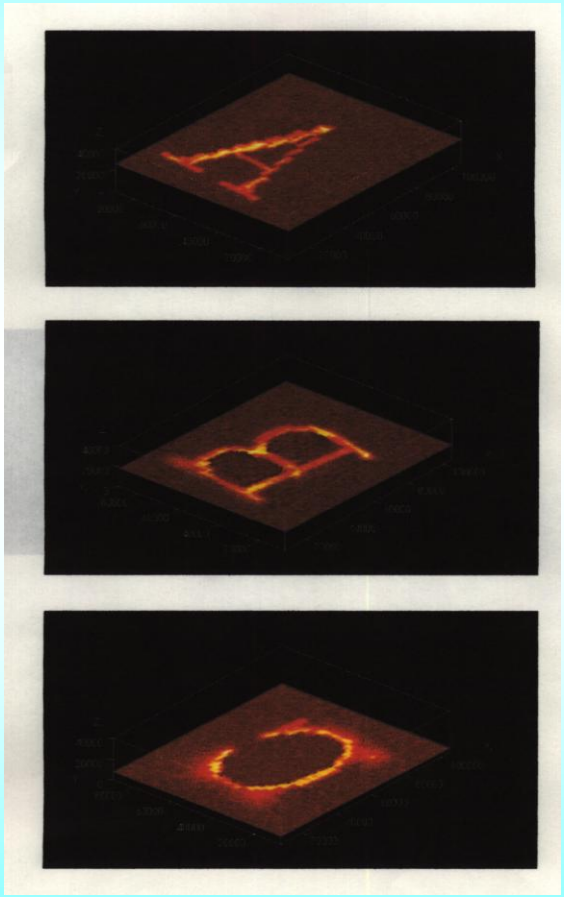


ESR spectra of Eu^{3+}-doped ZBLAN glass before (a) and after (b) the femtosecond laser irradiation and the spectrum (c) of a Eu^{2+} -doped AlF_3-based glass sample

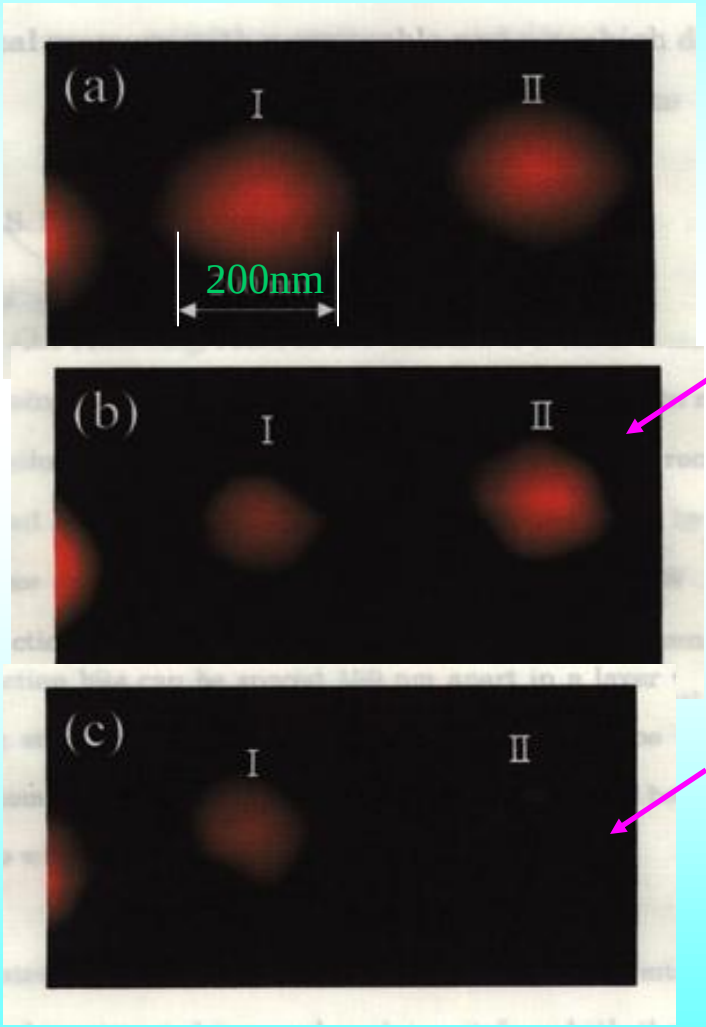


Potoluminescence spectra of a Sm^{3+}-doped borate glass before and after the femtosecond laser irradiation

3D rewriteable memory using valence state change of Sm ion



Three layers spaced 2μm



4f-4f Sm^{2+}
692nm

fs
488nm Ar^{+}

fs + 514nmAr^{+}
488nm Ar^{+}

Appl. Phys. Lett., 80(2002)2263.

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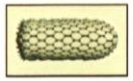

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In brief: Writing memories in light

Three-dimensional memories offer the potential for incredibly high data storage densities, but creating a rewritable 3D memory medium has proved tricky. Now a group of Japanese researchers have developed an all-optical rewritable memory material with a capacity of 10 Tbit cm^{-3}.

11 April 2002

Jonathan Dawid

Three-dimensional optical memories, which store data on multiple planes in a transparent medium, offer incredibly high storage capacities – as much as several terabits in a block the size of a sugar cube. (1 Tbit = 10^{12} bit, equivalent to 200 CD-ROMs.) But although several suitable materials have been demonstrated that are suitable for read-only purposes, the ability to selectively erase and rewrite information has proved much harder to achieve. Now, writing in *Applied Physics Letters*, Miura, Qiu, Fujiwara, Sakaguchi and Hirao demonstrate a high-capacity 3D memory that can be written, read, erased and rewritten using all-optical methods.

The material in question is glass doped with ions of samarium, a rare-earth metal. These can be switched between two stable valence states, Sm^{3+} and Sm^{2+}, by photoreduction and photo-oxidation respectively,

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In brief: Writing memories in light

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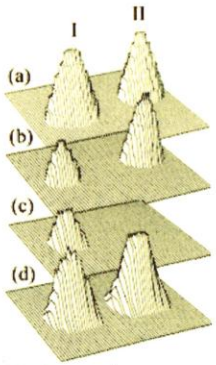


Distributions of photoluminescence intensity, showing selective erasure and rewriting of two neighbouring bits spaced 200 nm apart. **a**, Both bits in the photoreduced (Sm^{2+}) state. **b** and **c**, after 'erasing' bits I and II respectively by photo-oxidation with a continuous-wave laser. **d**, After 'rewriting' both bits using photoreduction by femtosecond laser irradiation.

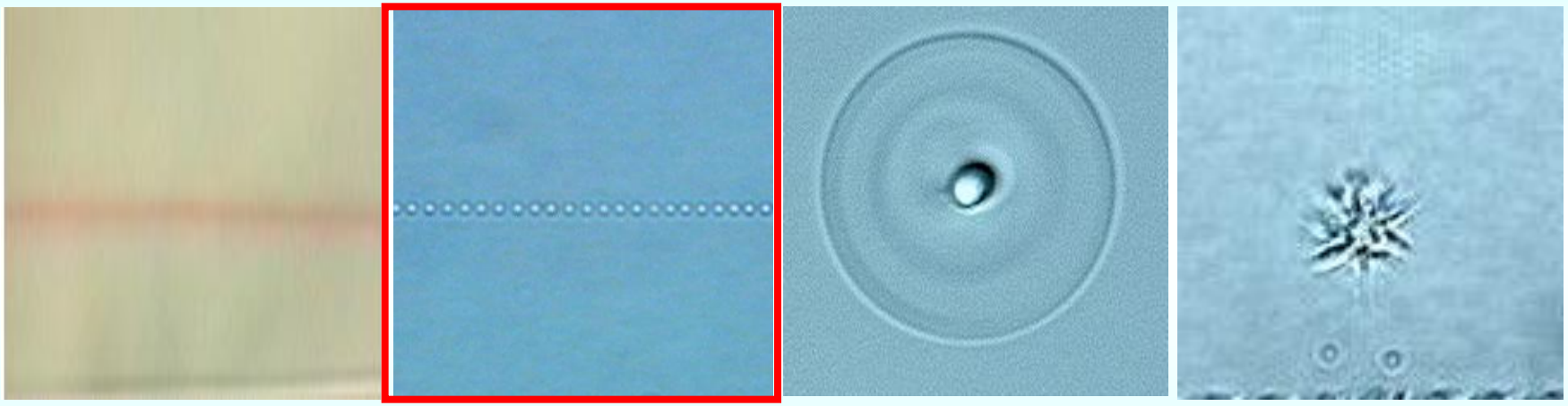
and are distinguished by their different photoluminescence spectra. This combination of properties allowed the authors to develop an all-optical memory device in which bits are represented by the ionic valence state. Femtosecond laser pulses are used to 'write' bits by photoreducing Sm^{3+} to Sm^{2+}, whereas to 'erase' the bit, the ions are photo-oxidized back to the 3+ state with a continuous-wave laser. Read-out is achieved using a weaker laser to excite a photoluminescence peak of the Sm^{2+} species that is completely absent in Sm^{3+}, giving excellent signal-to-noise characteristics and allowing bits to be packed very close together. Crucially, the physical independence of neighbouring bits makes it possible to store information in three dimensions, which the authors demonstrate by recording three separate images on planes spaced 2 μm apart. Because each bit can be made with an in-plane diameter of only 150 nm, this corresponds to an information storage density of 10 Tbit cm^{-3}.

Three-dimensional optical memory with rewriteable and ultrahigh density using the valence-state change of samarium ions

We report the recording, readout, and erasure of a three-dimensional optical memory using the valence-state change of samarium ions to represent a bit. A photoreduction bit of 200 nm diam can be recorded with a femtosecond laser and readout clearly by detecting the fluorescence as a signal

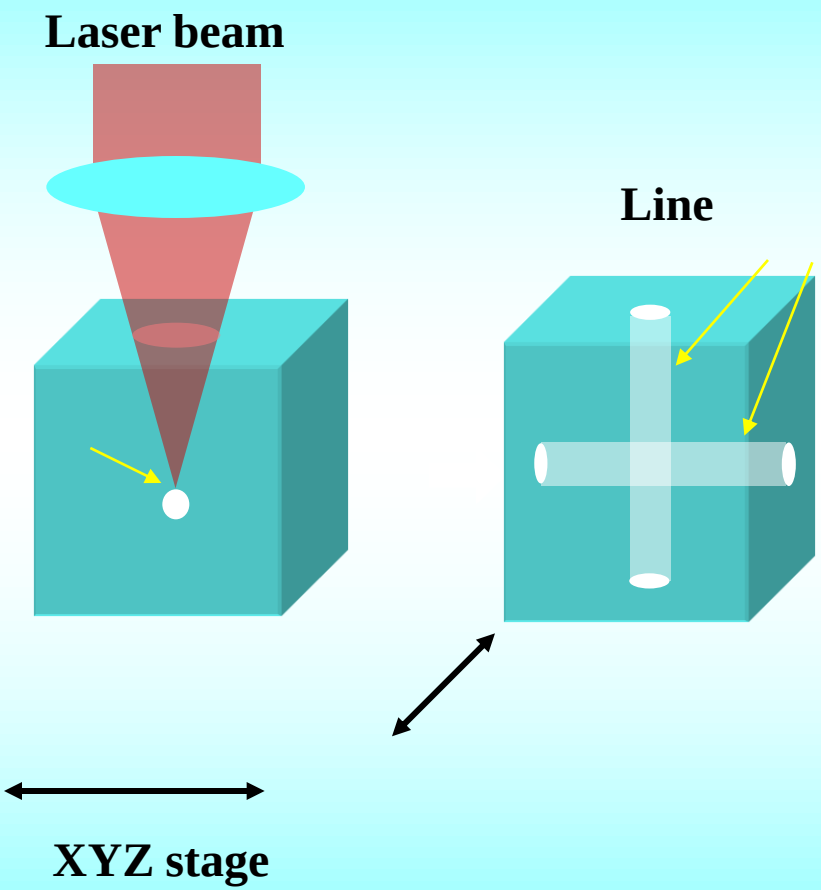
http://www.nature.com/cgi-taf/Gateway.taf?g=3&file=/materials/highlights/articles/m020411-3.html&filetype=&_UserRefe

Femtosecond laser induced microstructures



Various structures induced by
800 nm, 120fs laser-pulses

Femtosecond laser direct writing



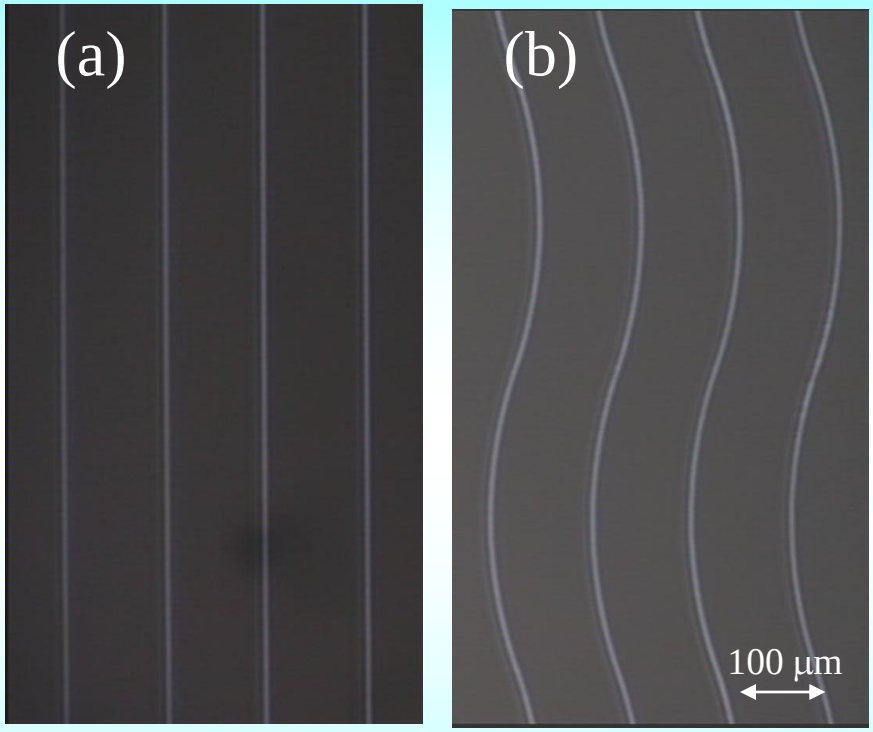
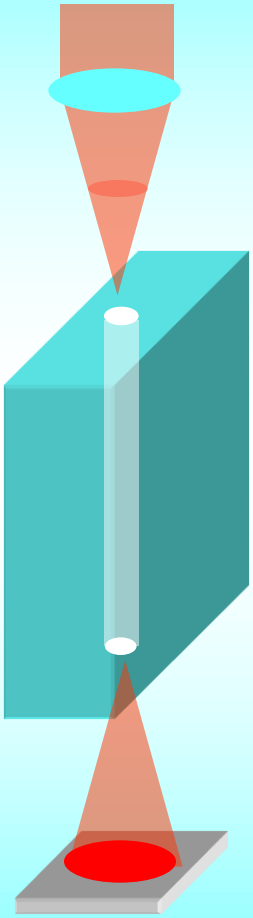
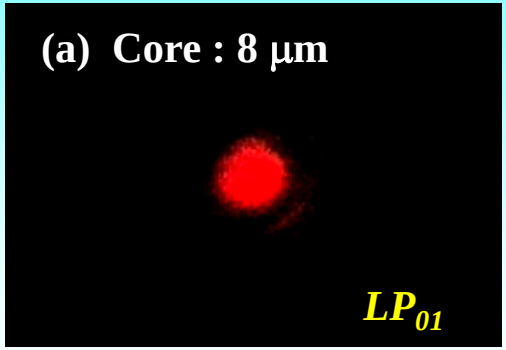
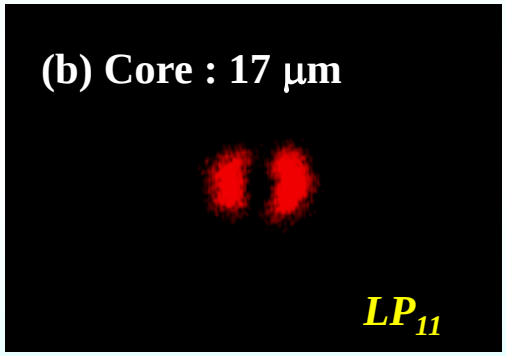


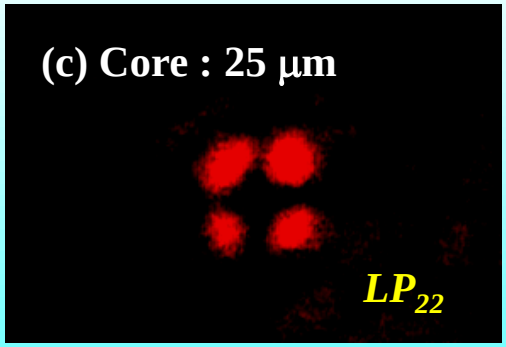
Photo-written lines in a glass formed using 800-nm 200-kHz mode-locked pulses. The lines were written by translating the sample (a) parallel or (b) perpendicular to the axis of the laser beam at a rate of 20 μm/s and focusing the laser pulses through a 10X or 50X microscope objective, respectively.

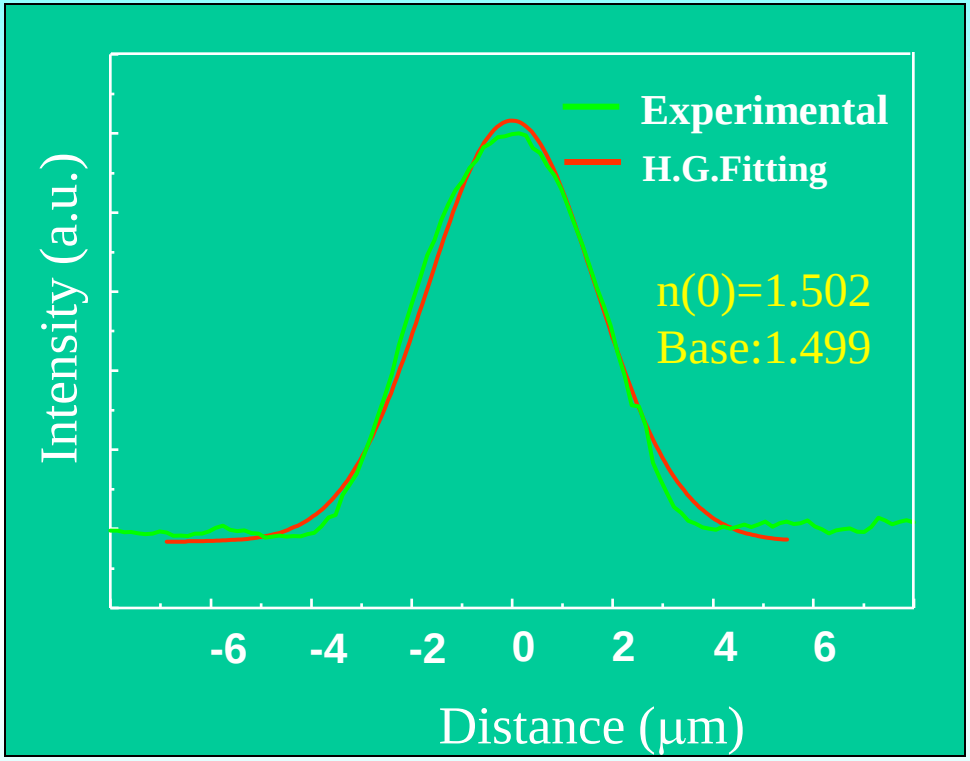
Mode-field patterns







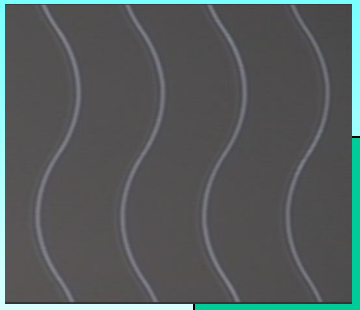


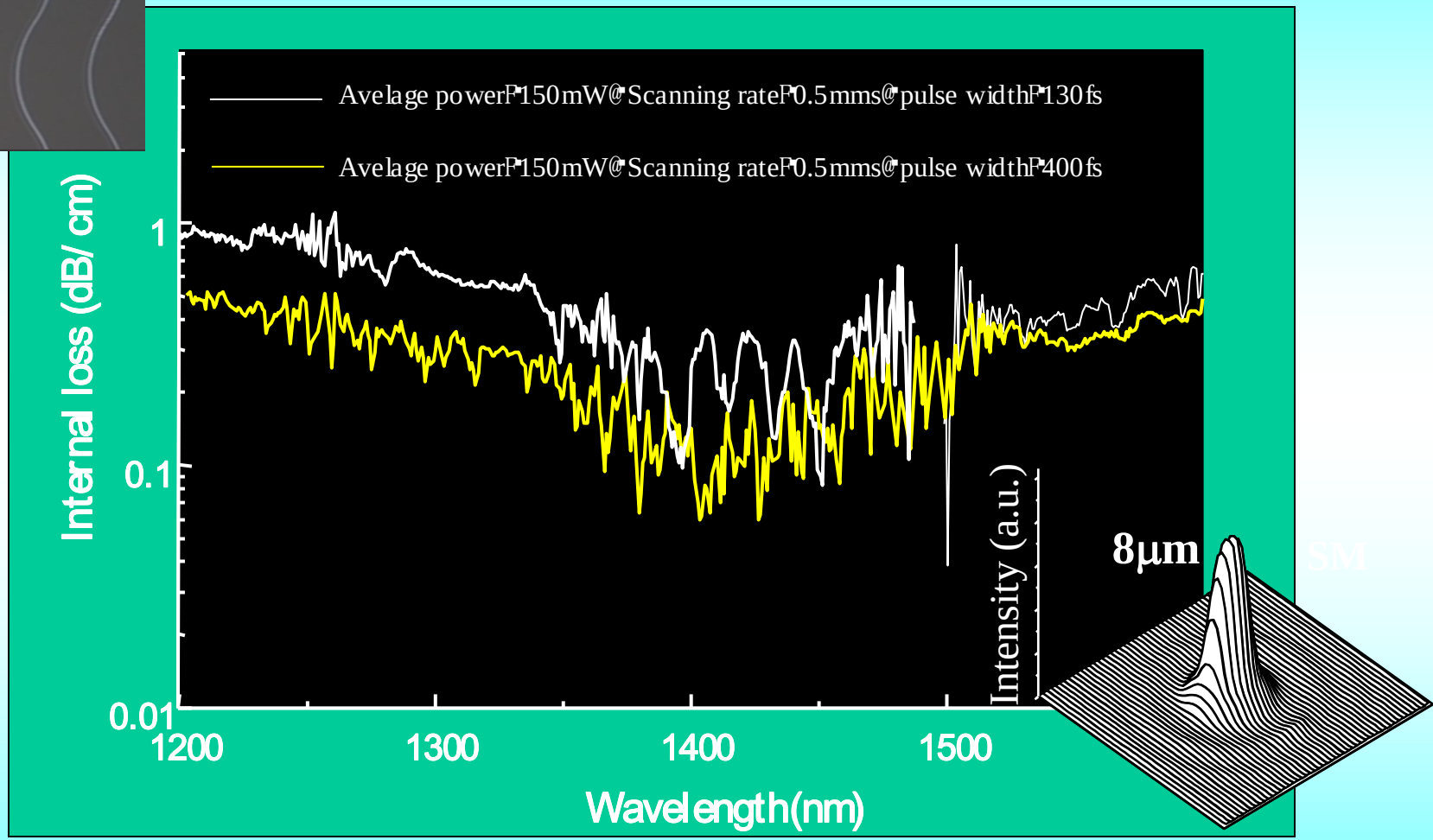


Result of Hermite-Gaussian fitting for the intensity distributions of the near field. The sample was the same as that observed in (a).The calculated result is almost in agreement with the experimental data, indicating that this waveguide is a graded-index type with a quadratic refractive-index distribution.

***Appl. Phys. Lett.*, 71(1997)3329.**

Internal loss of waveguides

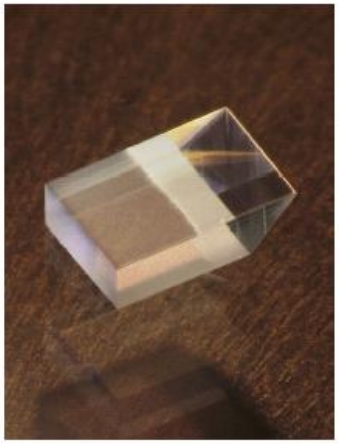


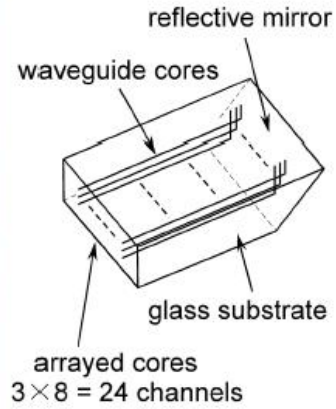


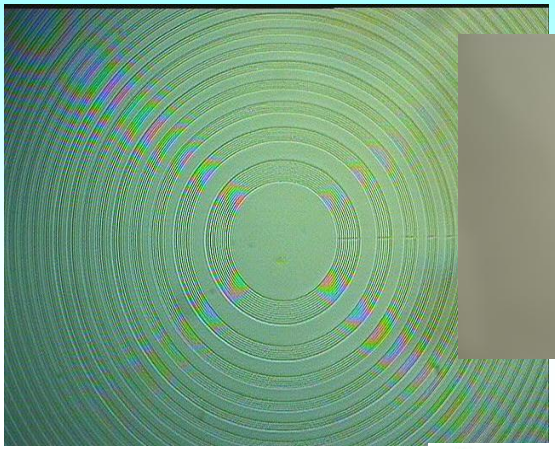
Appl. Phys. Lett., 71(1997)3329.

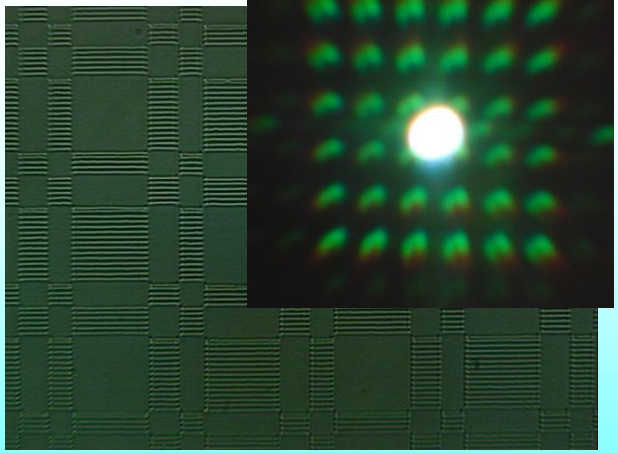
Internal loss of waveguides drawn by translating the silica glass perpendicular to the axis of the laser beam

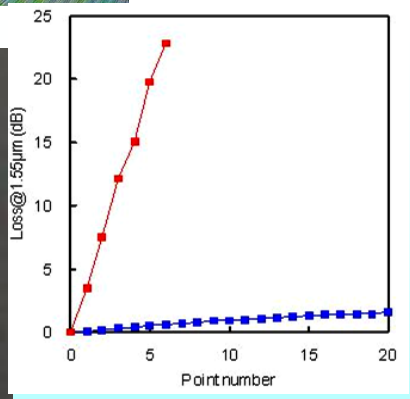
Direct writing of grating and lens









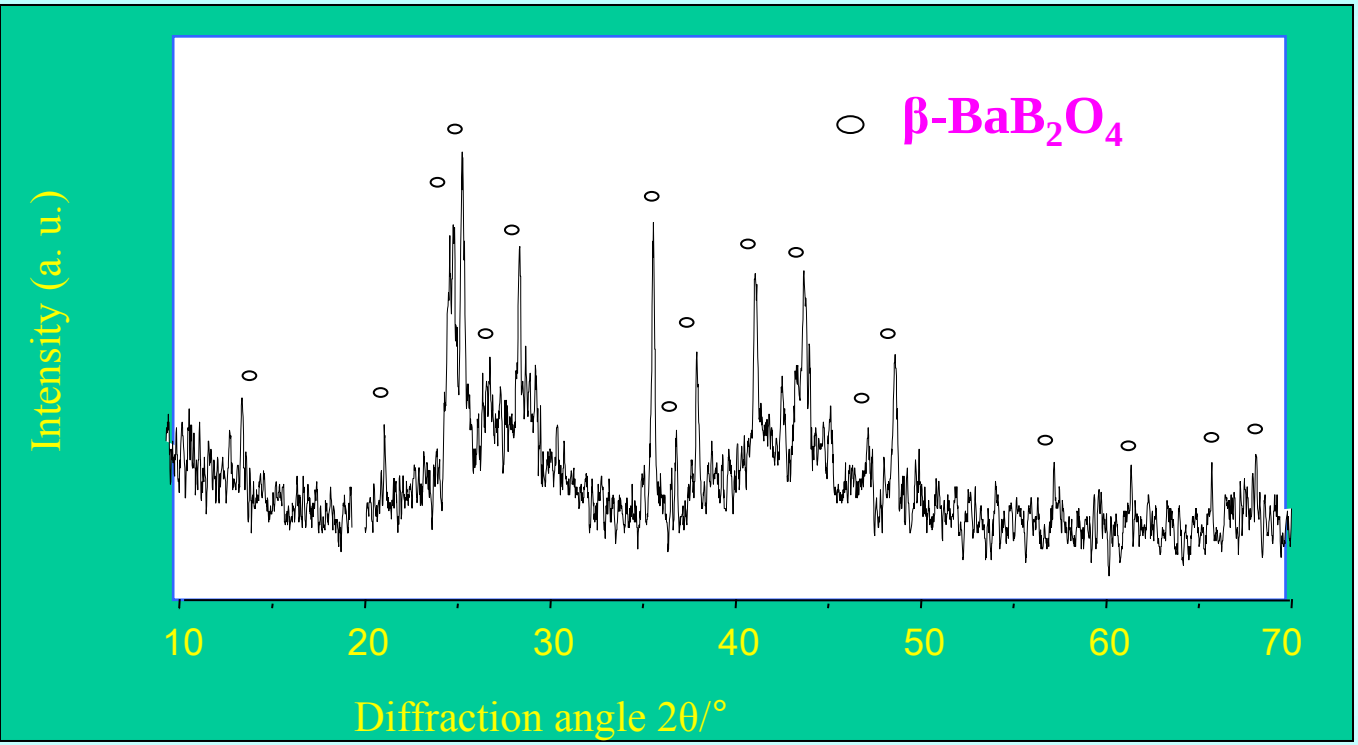


Appl. Phys. Lett., 71(1997)3329.

Opt. Lett., 29(2004)2728.

Precipitation of functional crystal

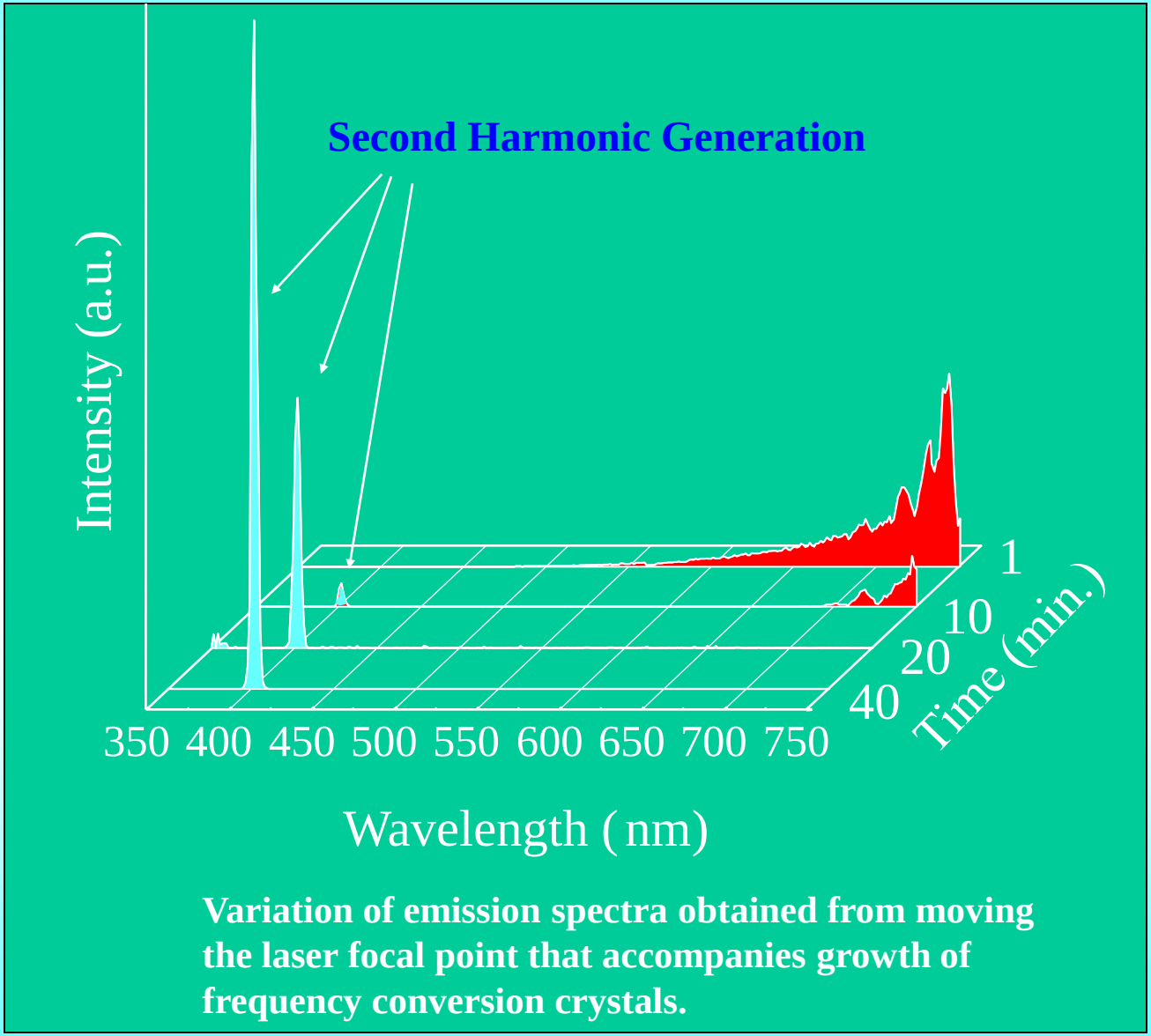
Fs laser with high repetition rate=Local heat source



XRD pattern

Photograph

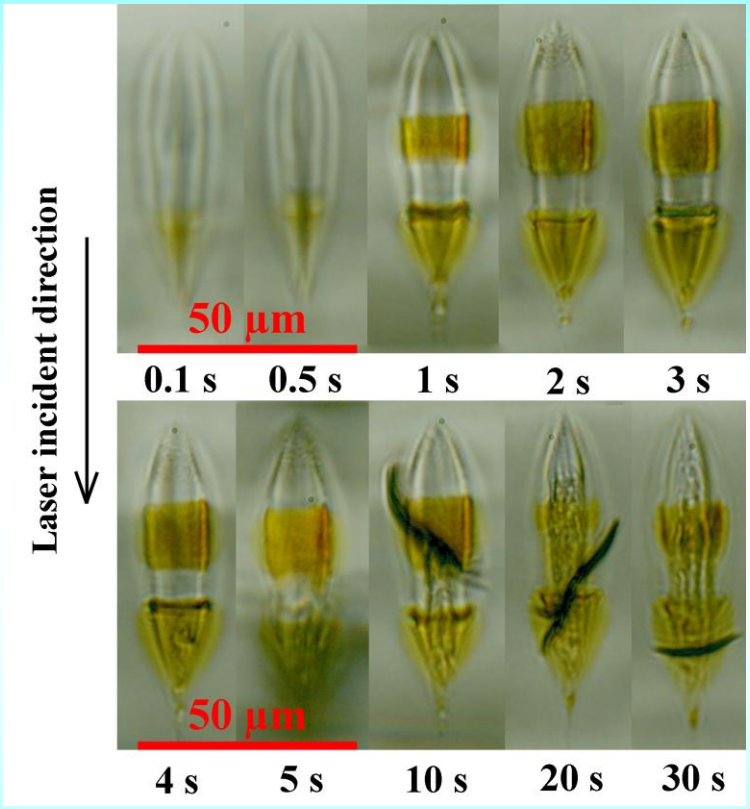
Opt. Lett., 25(2000)408.

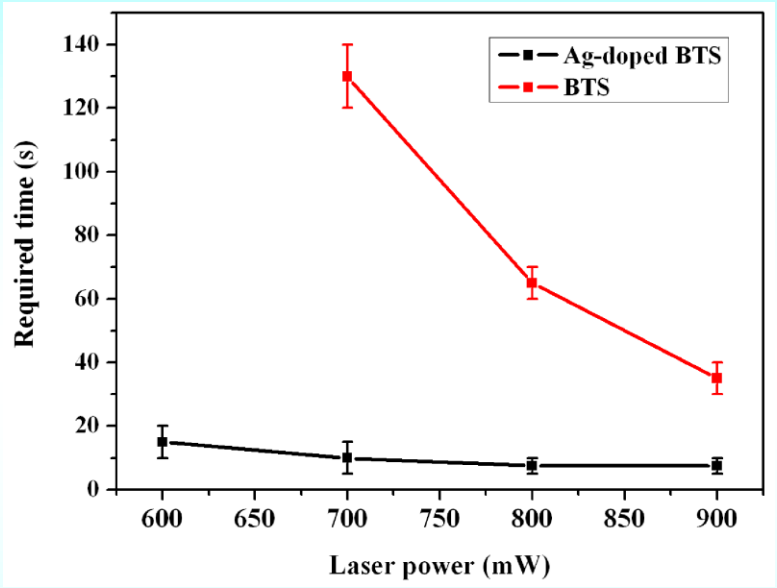


Variation of emission spectra obtained from moving the laser focal point that accompanies growth of frequency conversion crystals.

Effect of Ag^+ on fs laser induced precipitation of crystals

Opt. Lett., 34(2009)1666.





Micrographs of side-view of the focal regions illuminated by natural light after femtosecond laser irradiation (laser power: 900 mW, irradiation time: 0.1-30 s).

Dependence between the required time for crystallization and the laser power in Ag+-doped BTS glass and BTS glass.

3D microdrilling of photosensitive glasses

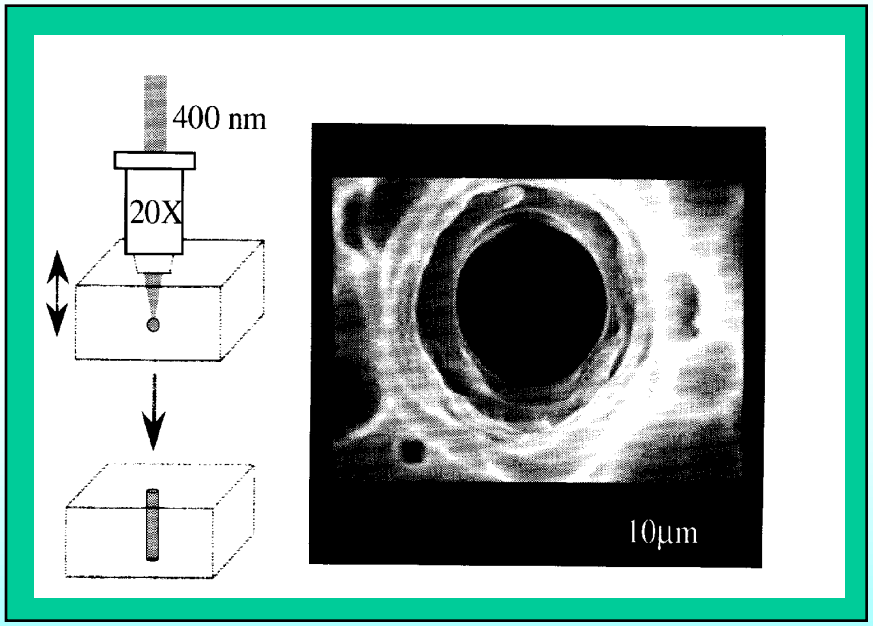
(developed by Dr. Stookey)

$Ag^{+} \longrightarrow Ag$

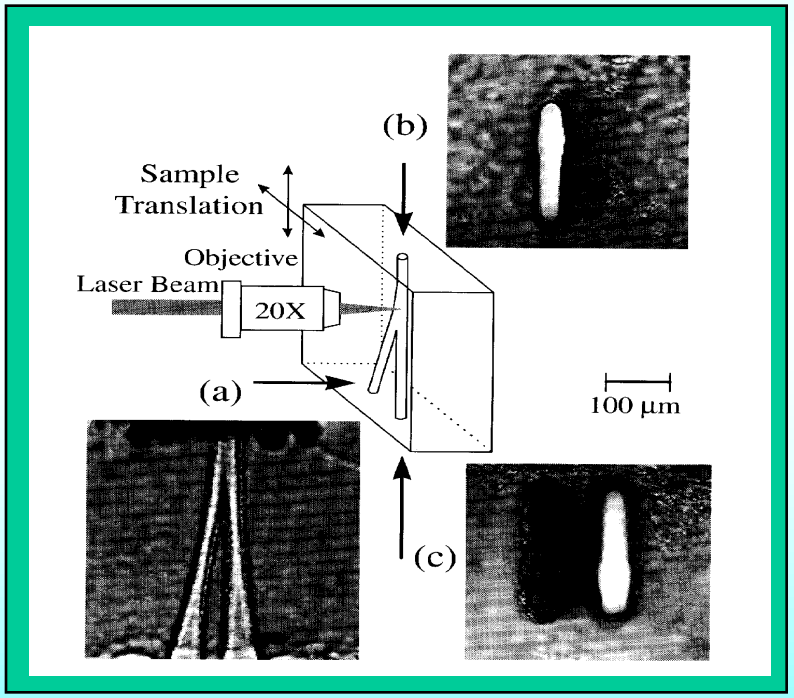
$nAg \longrightarrow Ag_n$

$Vc \gg Vg$

in diluted HF solution



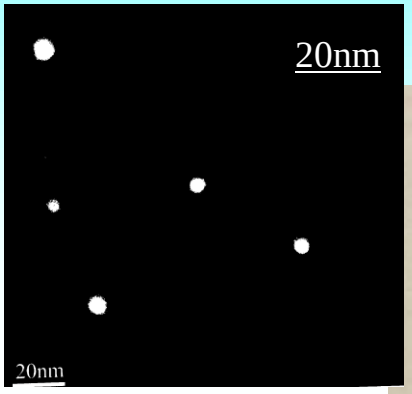
Straight hole



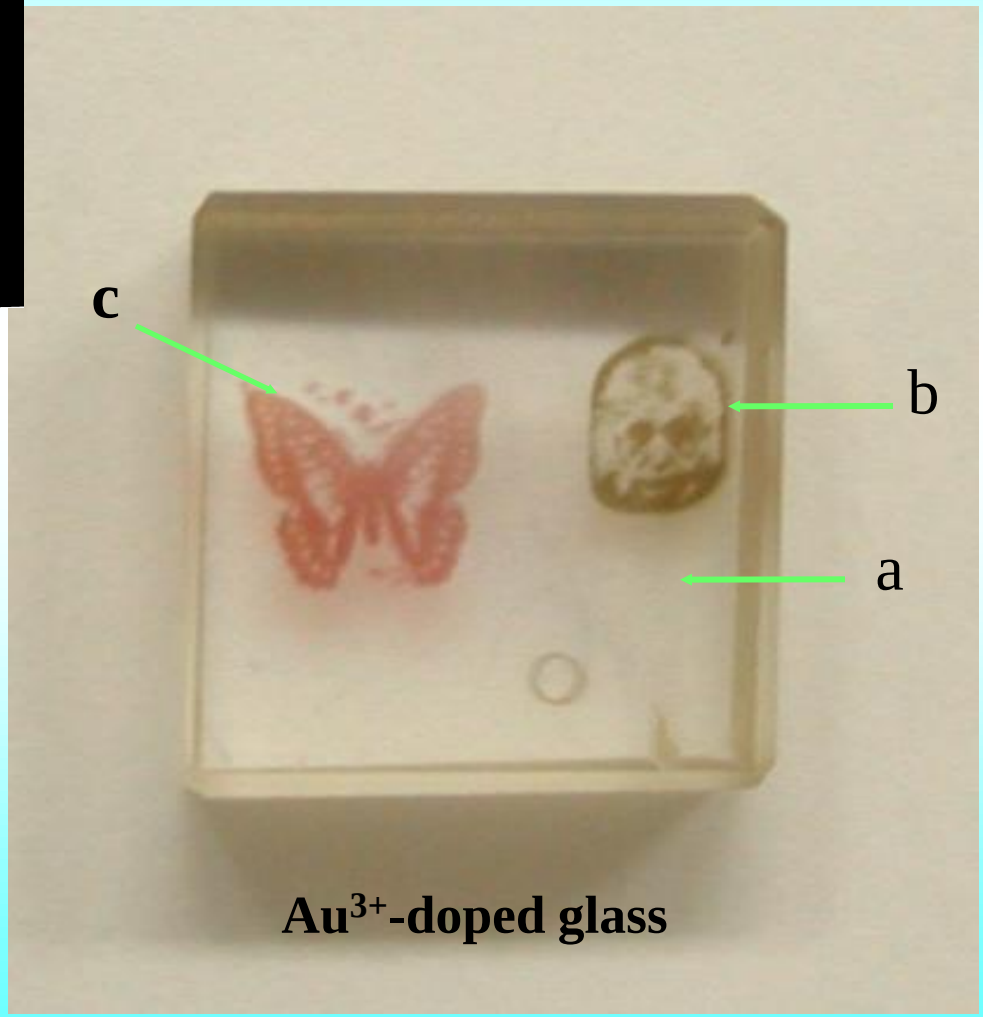
Y-branch holes

***Jpn. J. Appl. Phys.*, 38(1999)L1146.**

Space-selective precipitation of nanoparticles



Angew. Chem. Int. Ed., 43(2004)2230.



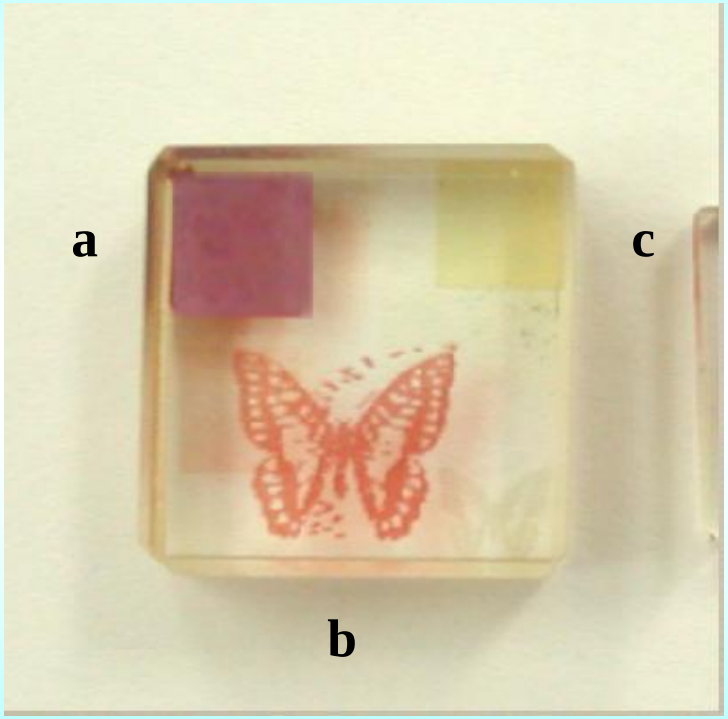
a:before irradiation

b:after irradiation

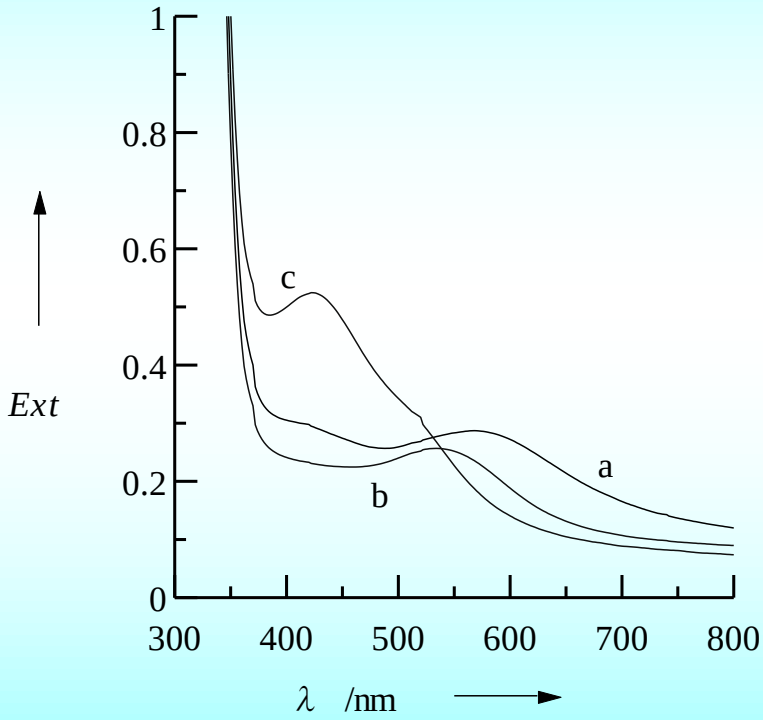
c: after annealing at 550℃ for 10min

Size control of precipitated Au nanoparticles

Angew. Chem. Int. Ed., 43(2004)2230.



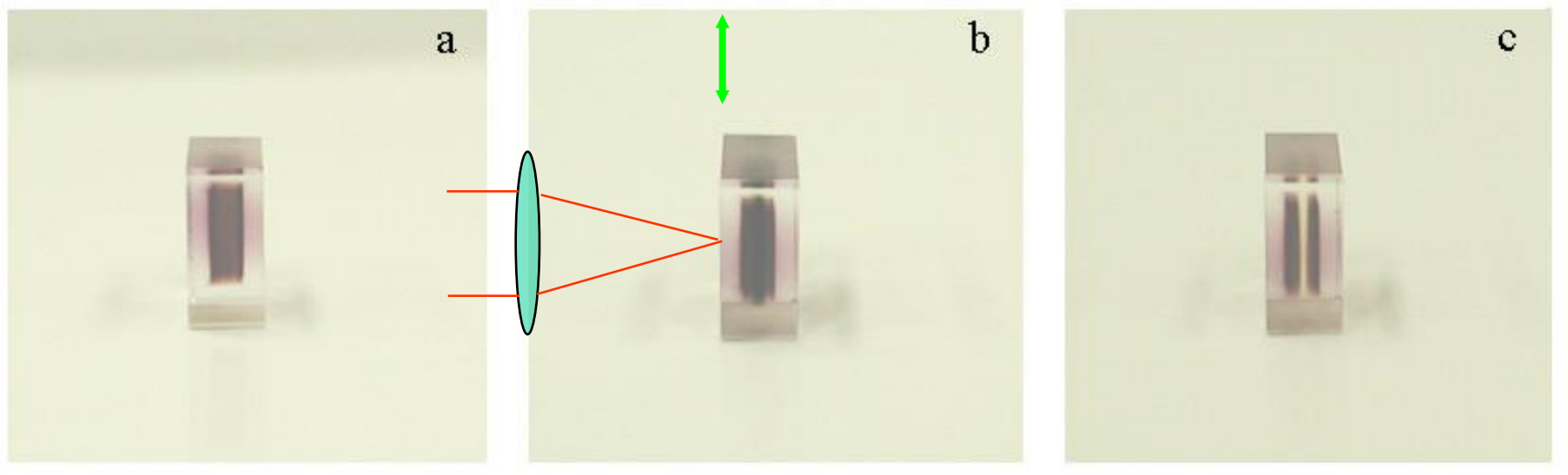
a: 6.5 x 10^{13}W/cm^2
b: 2.3 x 10^{14}
c: 5.0 x 10^{16}



Absorption spectra

Space-selective dissolution of Au nanoparticles

Angew. Chem. Int. Ed., 43(2004)2230.



a: before second laser irradiation

b: after second laser irradiation

c: after second laser irradiation and annealing at 300℃ for 30min

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Going dotty

Making a three-dimensional circuit is no easy task, however. At the moment, chip designers build them layer by layer, but this is a laborious process and it limits the designs that can be used. Now Jianrong Qiu, a physicist at the Shanghai Institute of Optics and Fine Mechanics, and colleagues from China and Japan have worked out a way to draw the desired circuit directly into a block of glass.

Three dimensions means faster chips and more memory.

© Angewandte Chemie

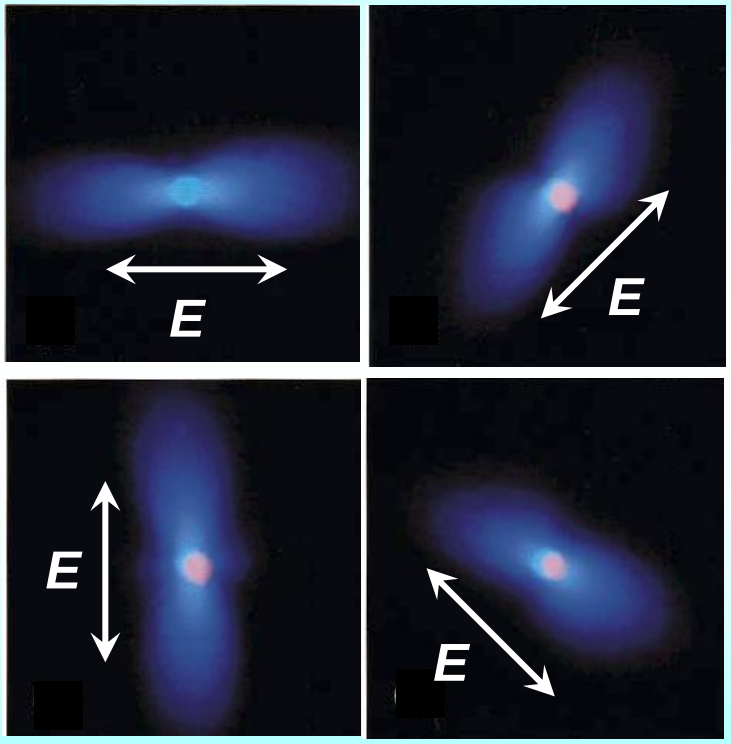
So far the researchers have used the technique to create three-dimensional images in the glass, such as the butterfly shown here. The 5-millimetre-wide image is made from millions of tiny balls of gold, each about seven nanometres across, which is roughly 10,000 times thinner than a human hair. The researchers report their results in the latest edition of the chemistry journal *Angewandte Chemie*[1].

It is even possible to erase

Making a three-dimensional circuit is no easy task, however. At the moment, chip designers build them layer by layer, but this is a laborious process and it limits the designs that can be used. Now Jianrong Qiu, a physicist at the Shanghai Institute of Optics and Fine Mechanics, and colleagues from China and Japan have worked out a way to draw the desired circuit directly into a block of glass.

Three-dimensional engrave in glass

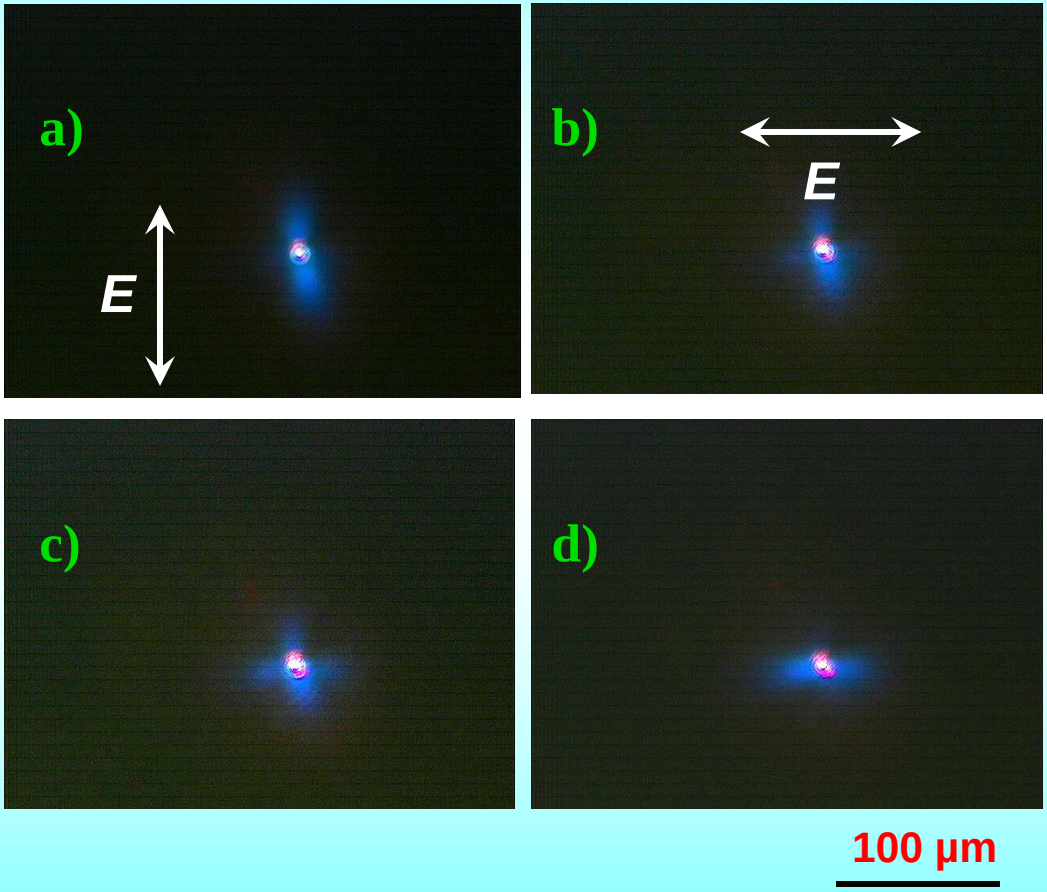
Novel femtosecond laser-induced phenomena



Polarization-dependent light scattering

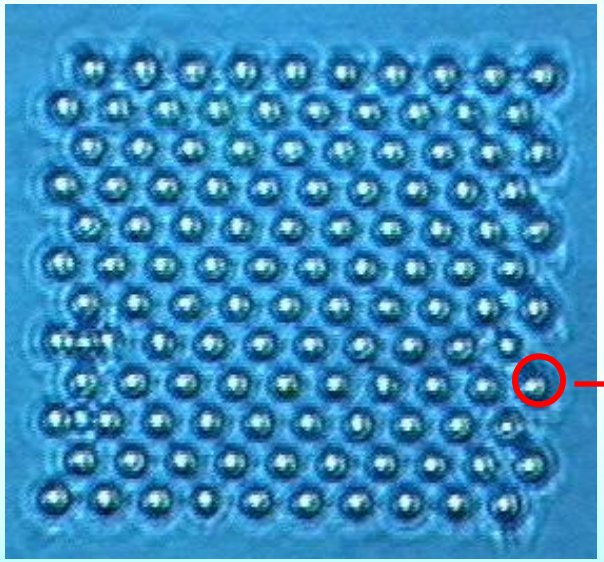
***Phys. Rev. Lett.*, 82(1999)2199.**

Memorized polarization-dependent light scattering in doped glasses and crystals



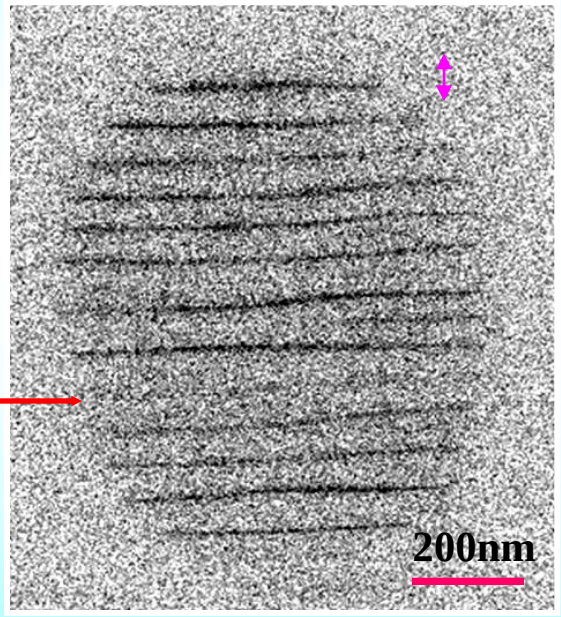
Appl. Phys. Lett., 77(2000)1940.

Single femtosecond laser beam-induced nanograting



Optical microphotograph

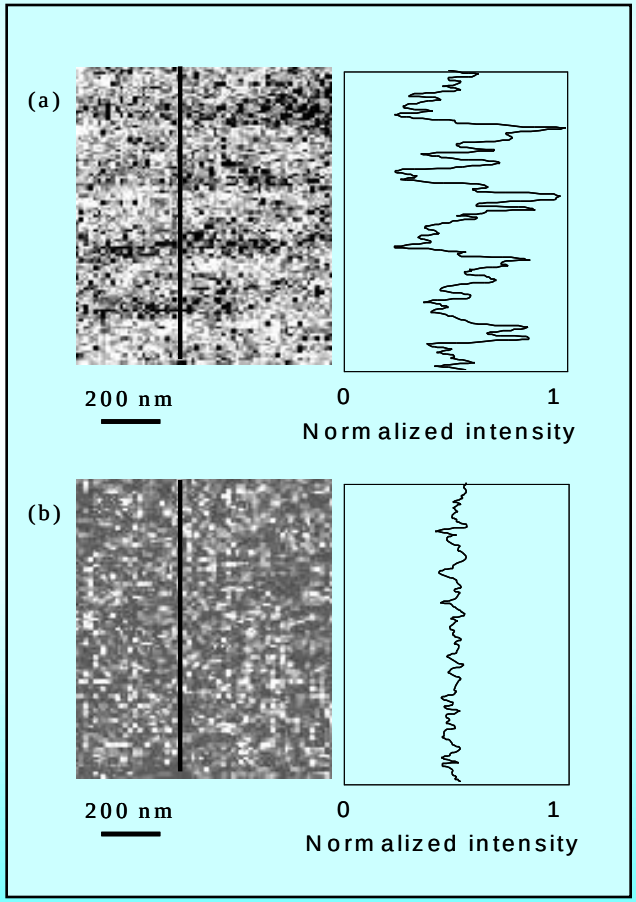
100× (0.95)
120fs
200kHz
200mW
1s



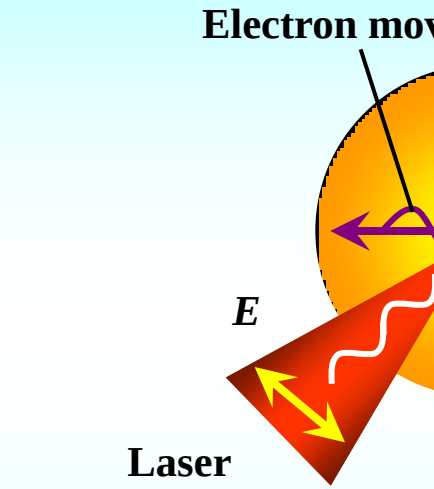
BEI image of SEM

Phys. Rev. Lett., 91(2003)247405.

Polarization-dependent femtosecond laser -induced nano-structure



O and Si concentration AES mapping



momentum conservation

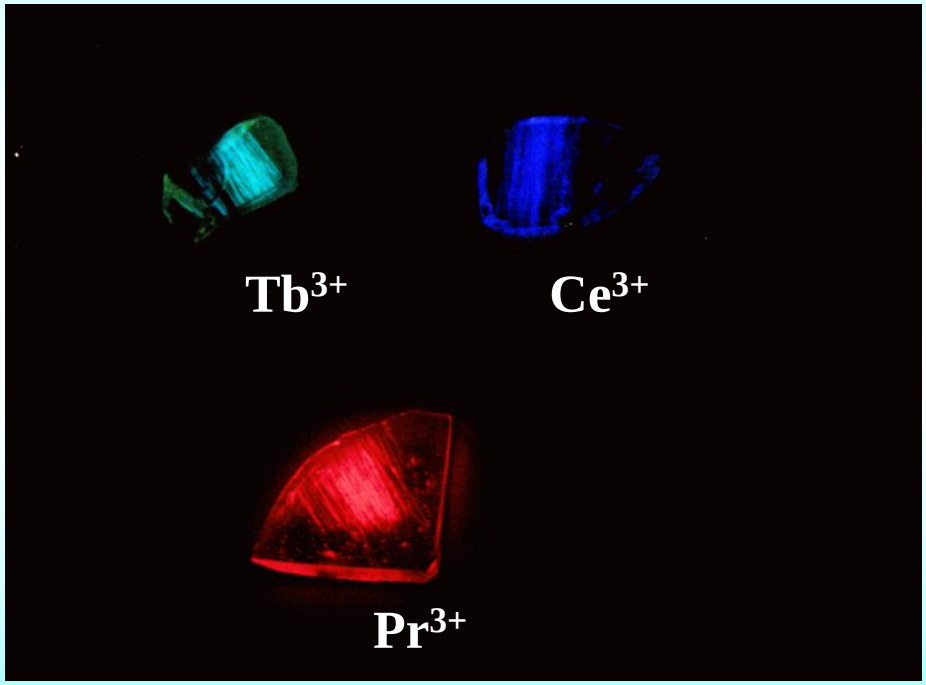
$$k_d = k_p - k_w$$

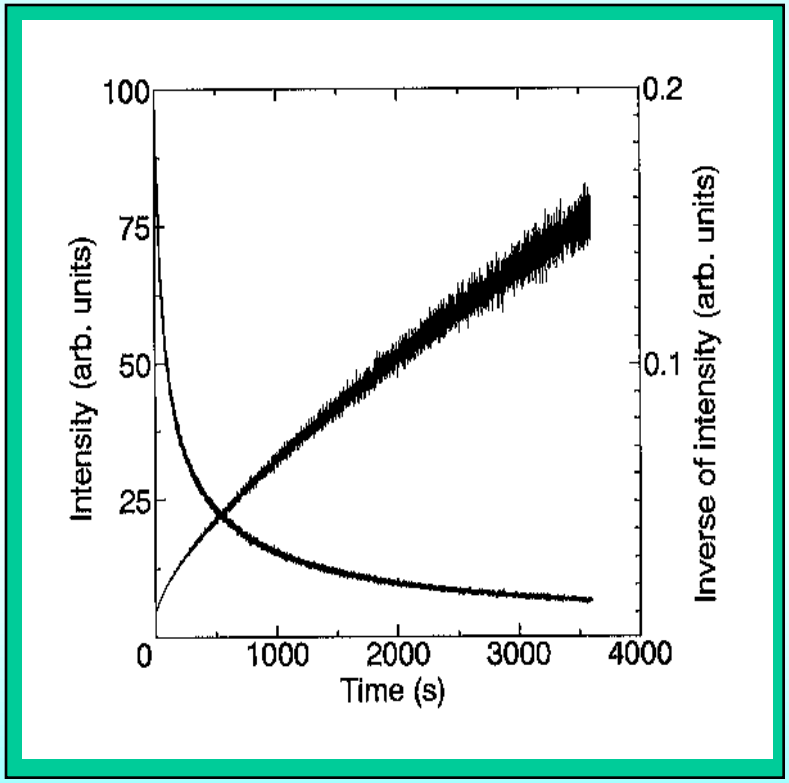
$$k_d = \frac{2\pi}{\Lambda}$$

k_w: laser wave vector
k_p: plasmon wave vector
k_d: dielectric constant modulation vector
Λ: period of nanostructure

Mechanism of the nanograting

Femtosecond laser induced long lasting phosphorescence

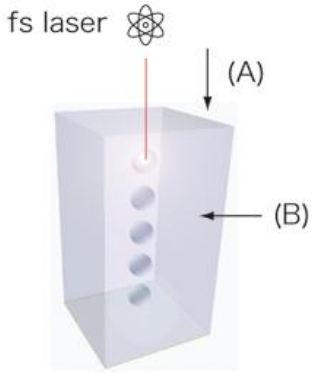


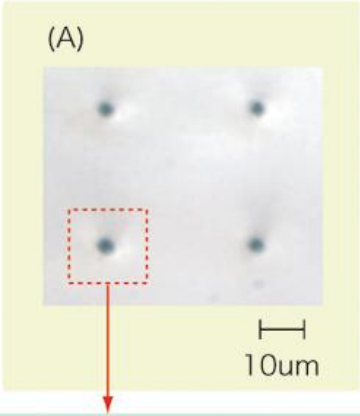


Decay curve of the phosphorescence at 543nm in the femtosecond laser irradiated Tb^{3+} -doped fluorozirconate glass

***Appl. Phys. Lett.*, 73(1998)1763.**

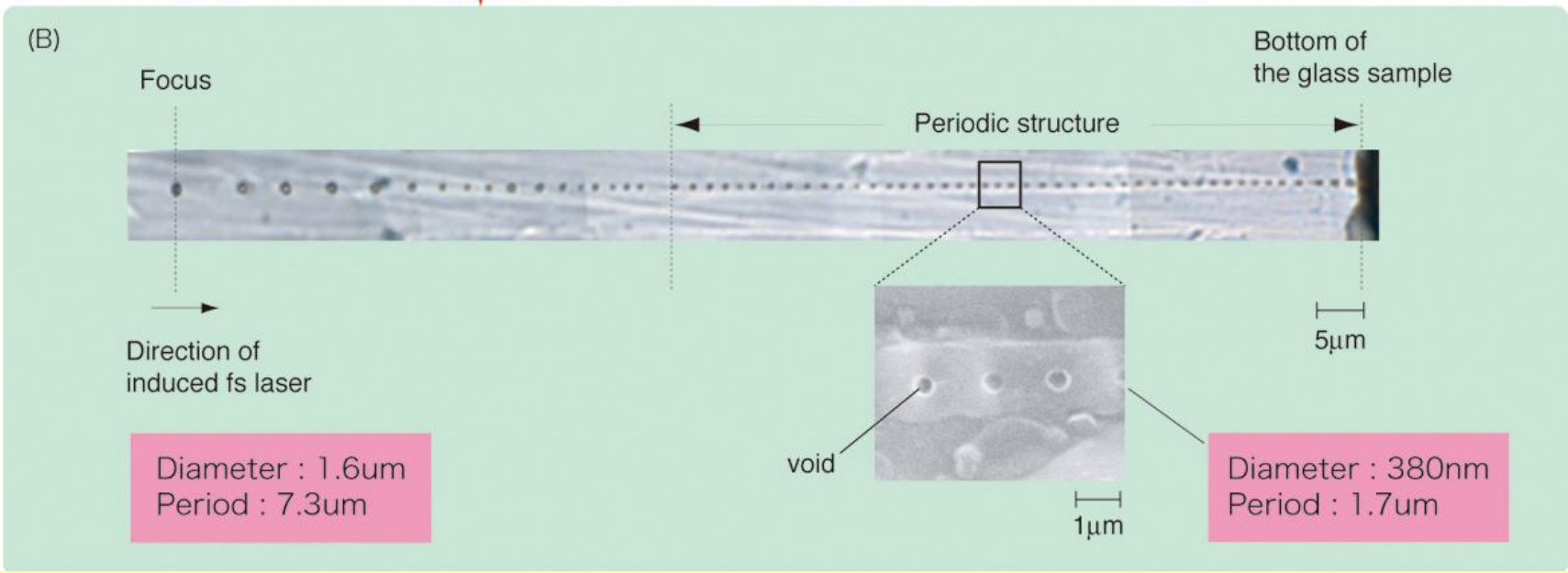
Fs laser-induced nano-void array





Condition :

Repetition rate : 1kHz
Pulse number : 250 pulses
Pulse energy : 10 uJ
Objectve lens : 100× (NA = 0.9)



***Nano Lett.*., 5(2005)1591.**

Non-paraxial nonlinear Schrodinger equation to exactly describe the pulse propagation:

$$\frac{\partial^2 E}{\partial z^2} + i2k\frac{\partial E}{\partial z} + \nabla_\perp E = kk''\frac{\partial^2 E}{\partial \xi^2} \underbrace{- ik\sigma(1+i\omega\tau_c)\rho E - ik\beta^{(K)}|E|^{2K-2}E - 2kk_0 n_2|E|^2 E}_{\text{Nonlinear effects}} \quad (1)$$

Electron density

$$\frac{\partial \rho}{\partial \xi} = \frac{1}{n^2}\frac{\sigma}{E_g}\rho|E|^2 + \frac{\beta^{(K)}|E|^{(2K)}}{K\hbar\omega} - \frac{\rho}{\tau_r}$$

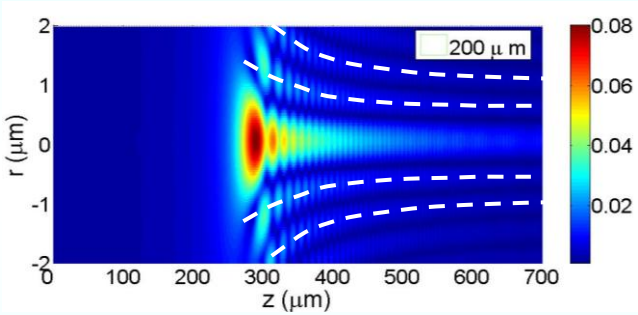
Analysis of interface spherical aberration by P. Török et al (electromagnetic diffraction th

$$I_0^{(e)} = \int_0^{\phi_{\max}} (\cos\phi_1)^{1/2}(\sin\phi_1)\exp\left[ik_0 \underbrace{\psi(\phi_1,\phi_2,-d)}_{\text{aberration function}}\right]\times(\tau_s+\tau_p\cos\phi_2)J_0(k_1 r_p \sin\phi_p \sin\phi_1)\times\exp(ik_2 r_p\cos\phi_p\cos\phi_2)\,d\phi_1 \quad (3)$$

***Appl. Phys. Lett.*, 92(2008)121113** .

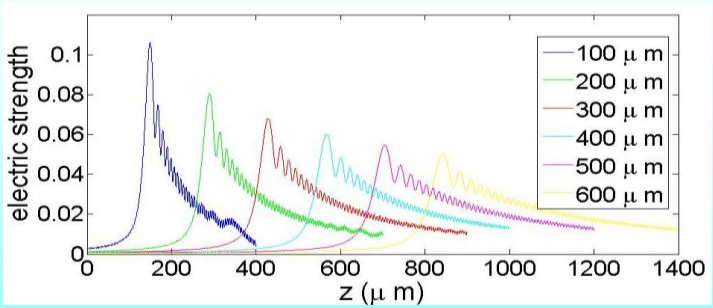
Fs laser-induced nano-void array

Self-aligned voids structure



Appl. Phys. Lett.,

92(2008)92904.

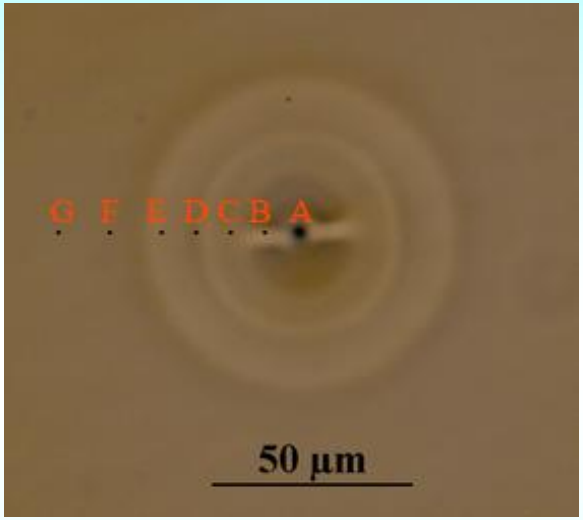


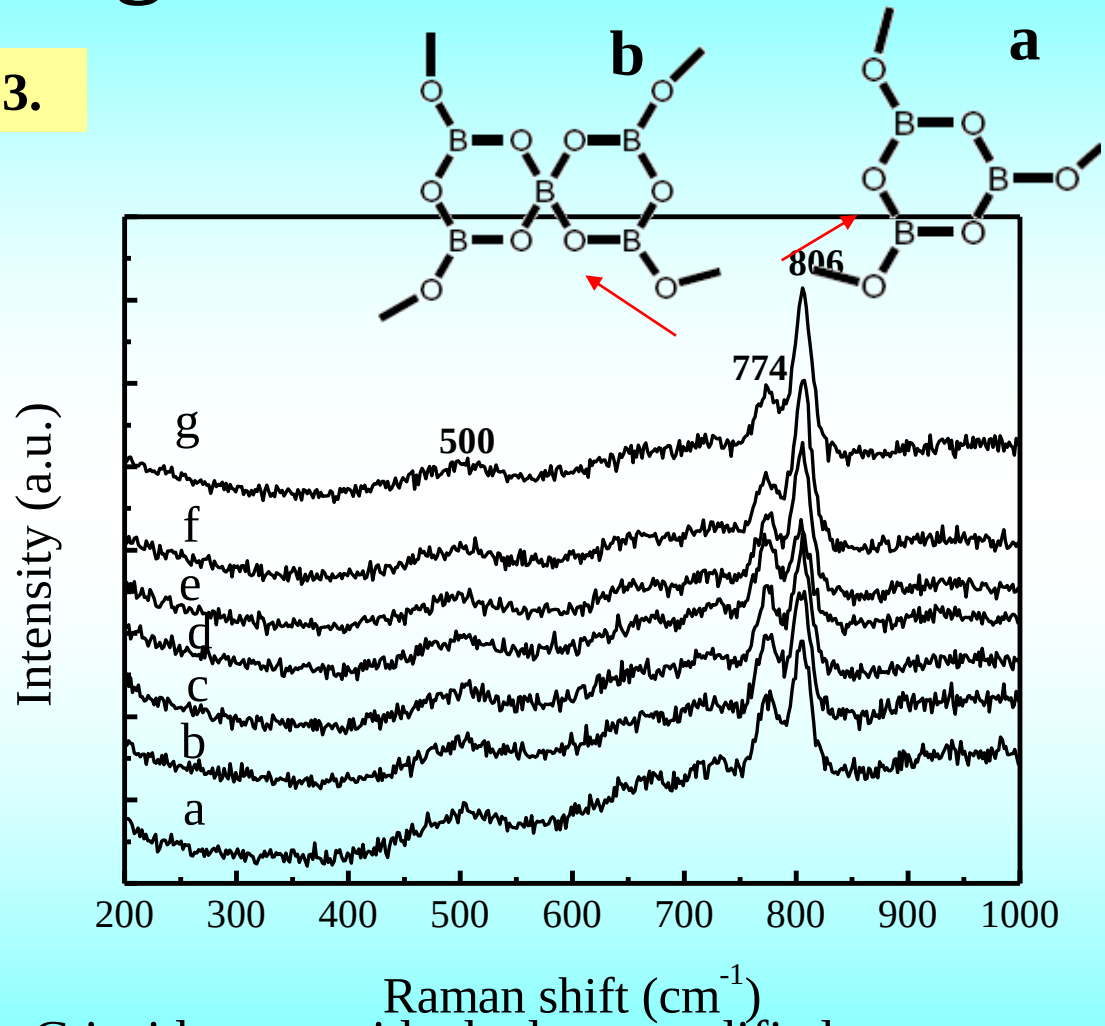
electromagnetic diffraction theory

On-axis electric strength distribution along the direction of the laser propagation (spherical aberration)

Coordination state change due to fs laser induced migration of ions

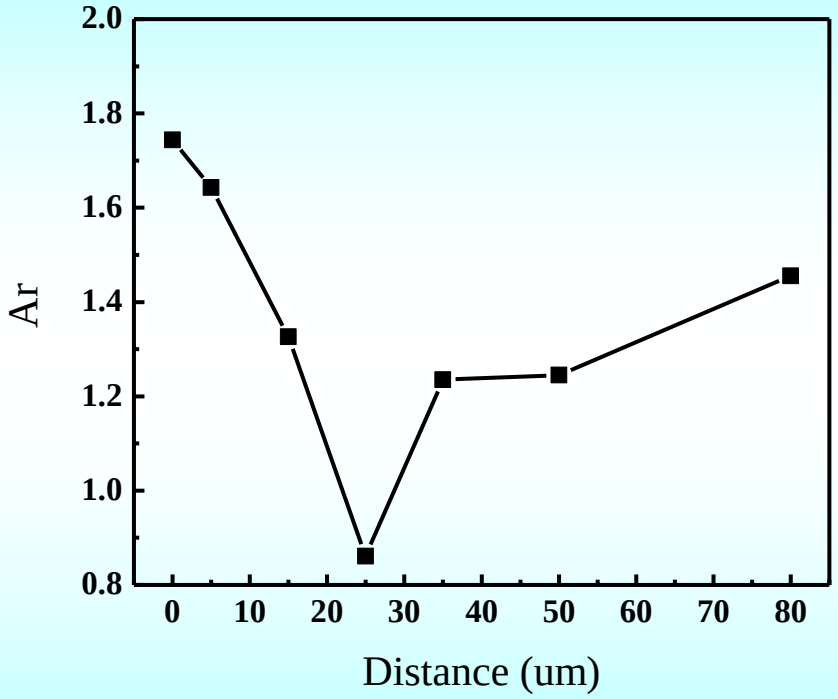
Appl. Phys. Lett., 92(2008)121113.





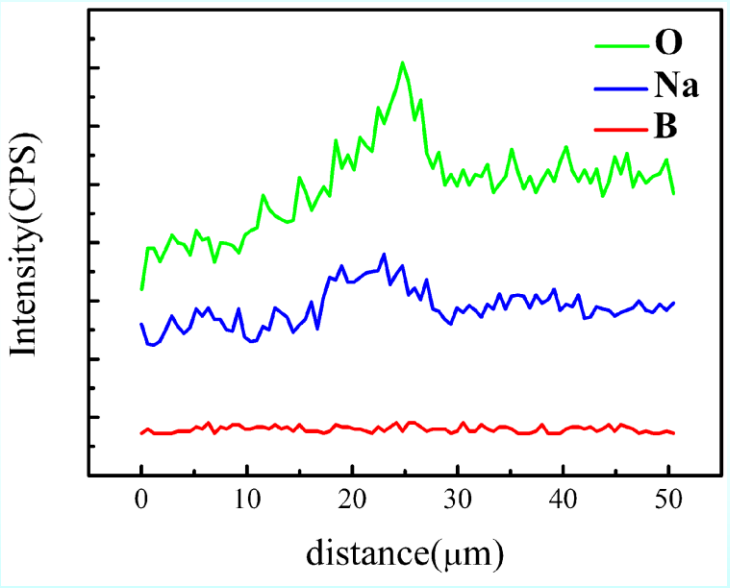
Different positions A–G inside or outside the laser modified zone shown in microscope images and their corresponding micro-Raman spectra a–g.

Coordination state change due to fs laser induced migration of ions



The relative integrated intensity Ar vs the distance from the central laser focal volume.

$$[BO_3]+ NBO+ Na^+ \rightarrow [BO_4]^-Na^+$$

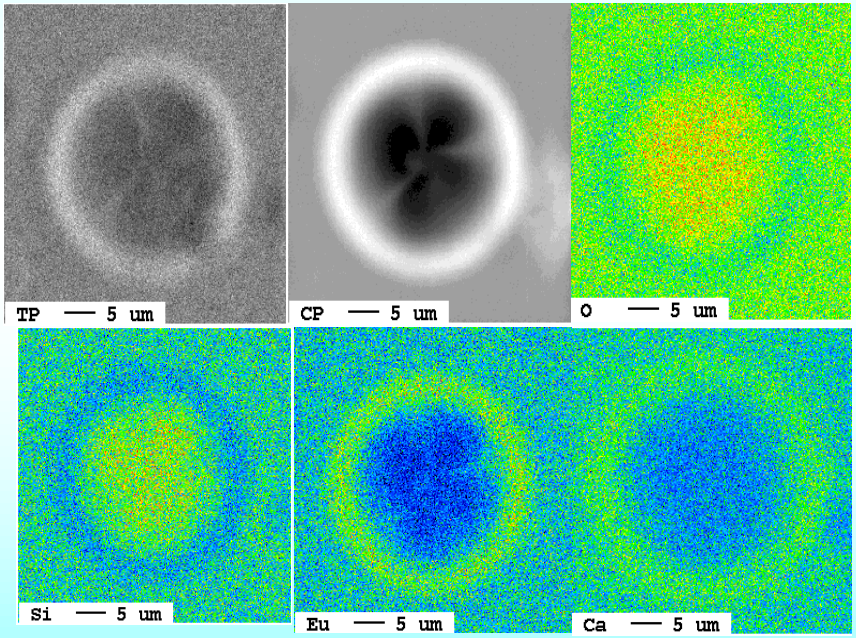


EDX line scanning spectra showing element distribution from the laser focal point to the edge of the laser modified zone.

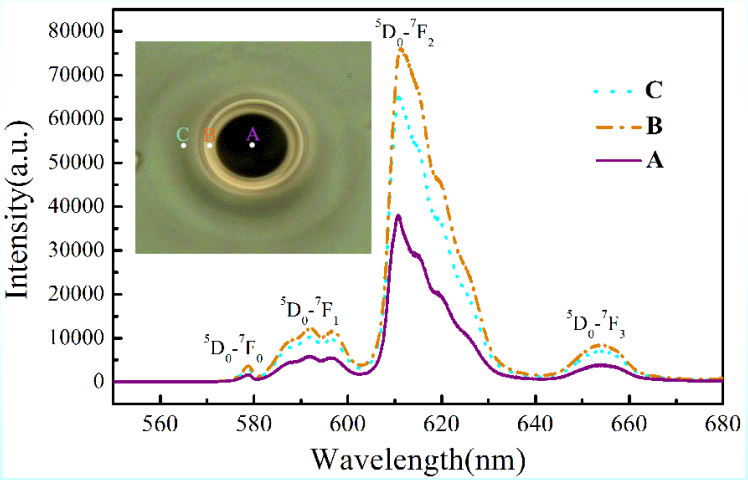
Fs laser induced migration of ions

$65SiO_2$-10CaO-$20Na_2O$-$5Eu_2O_3$

***Opt. Lett.*, 92(2009)121113.**



EDX line scanning spectra showing element distribution from the laser focal point to the edge of the laser modified zone.

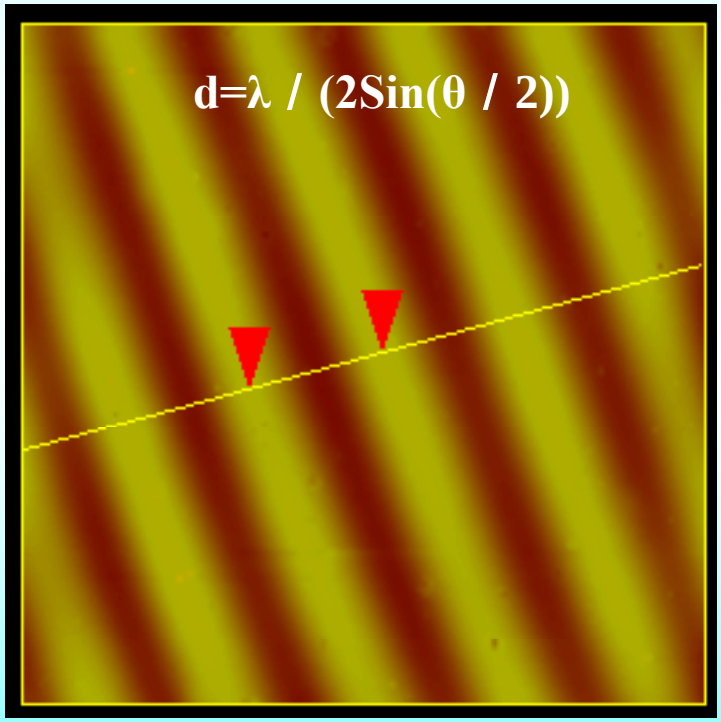


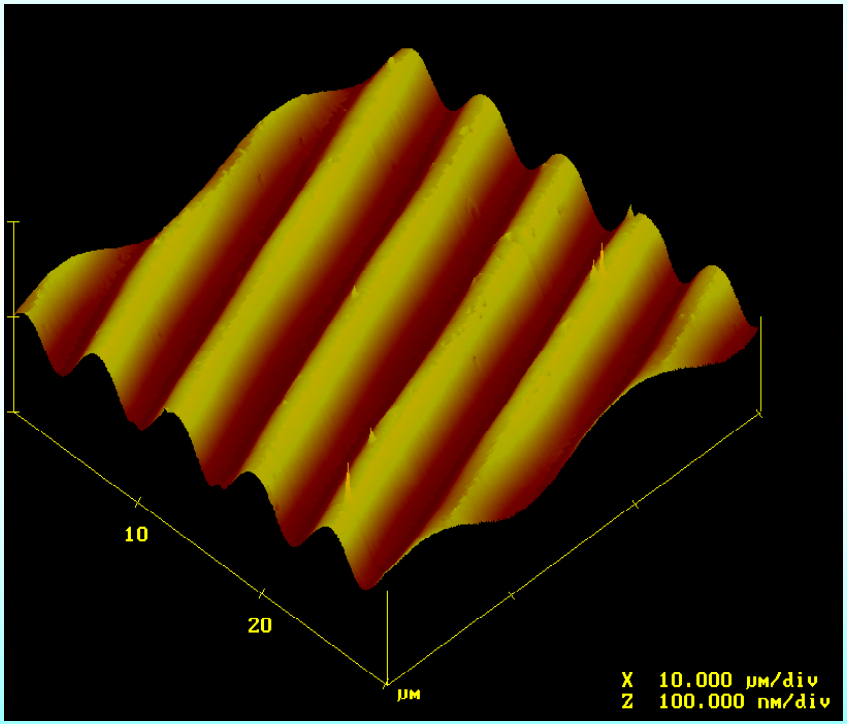
Confocal fluorescence spectra from different positions(A-C) of a laser modified zone.

AFM observation of micro-grating in glasses by coherent field of ultrashort pulsed lasers

(ω+ω)

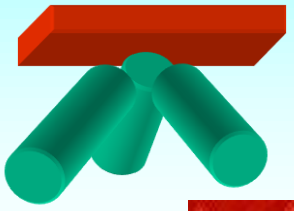
Appl. Phys. Lett., 77(2000)3887.



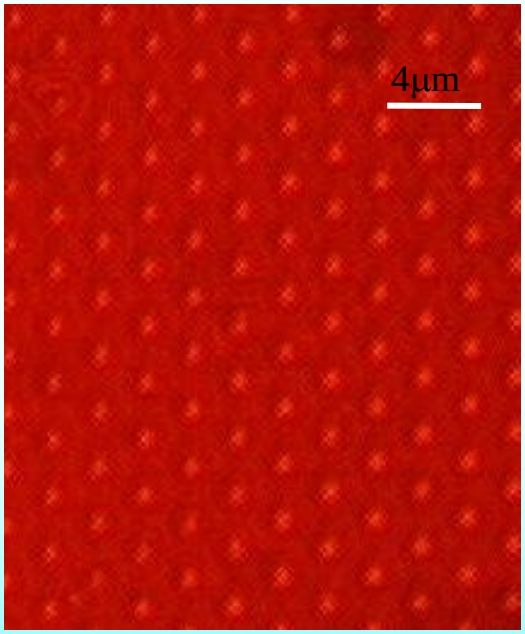


η > 90%

Observation of micro-grating in azobenzene polyimide by coherent field of ultrashort pulsed lasers



$(\omega+\omega+\omega)$



$\theta = 7°$

$d = 4\ \mu m$

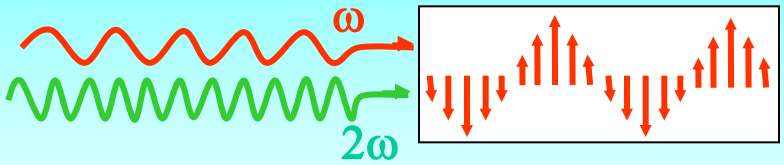
$\theta = 15°$

$d = 2\ \mu m$

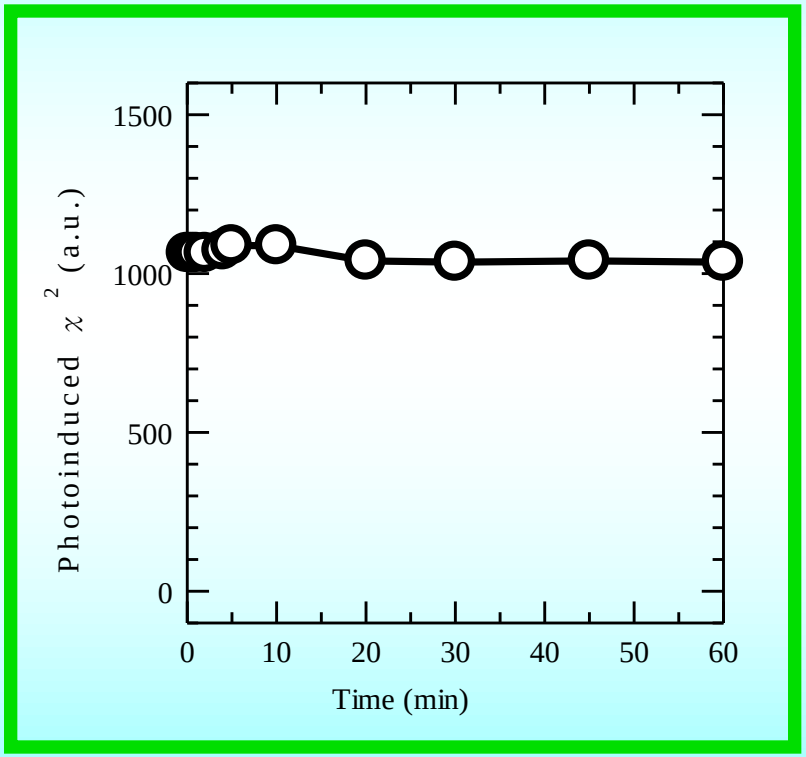
$\theta = 45°$

$d = 0.7\ \mu m$

All-optical poling (ω+2 ω)



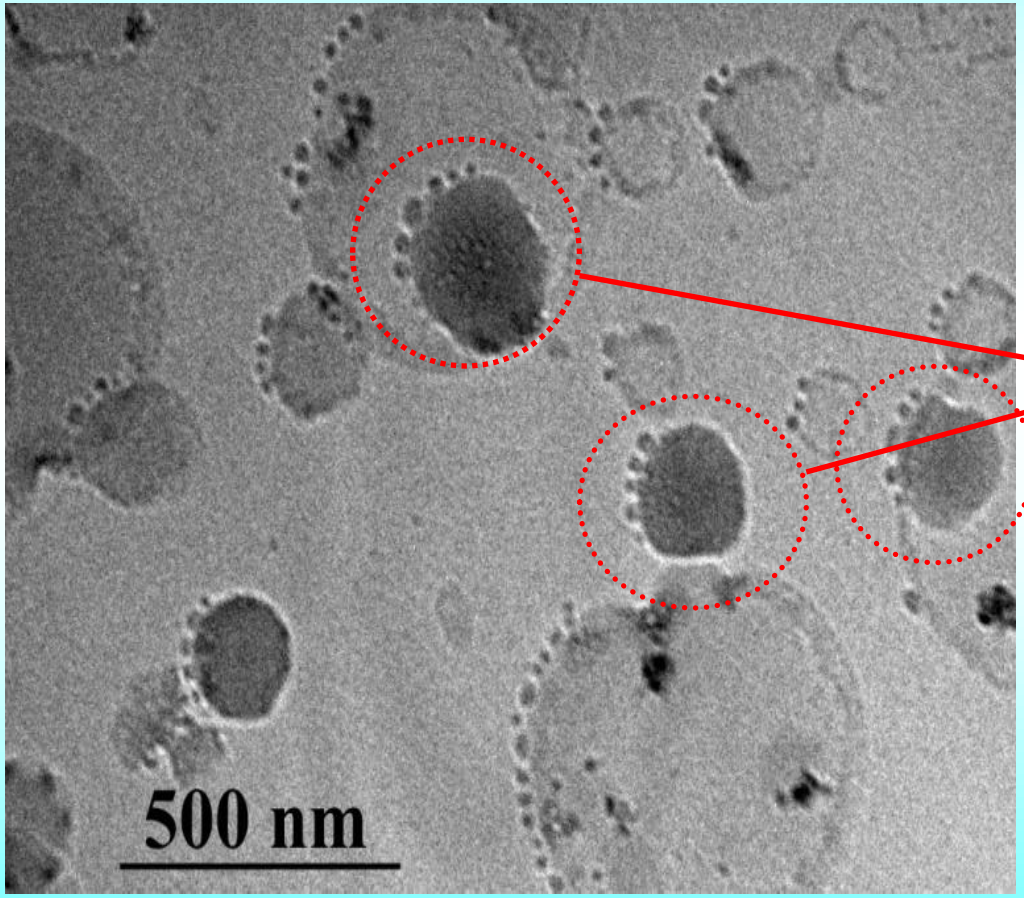
Photoinduced noncentrosymmetry $\chi^{(2)}$



***Opt. Lett.*, 26(2001)914.**

Non-linear coherent field induced large and stable second harmonic generation in chalcogenide glasses.

Micro structures looks like bear-paw induced by fs laser beam



Famous Chinese Dish
Bear-paw
（熊掌）

Conclusion

We have observed many interesting phenomena due to the interaction between femtosecond laser and transparent materials e.g. glasses.

We have demonstrated 3D rewritable optical memory, fabrication of 3D optical circuits, 3D micro-hole drilling, and 3D precipitation of functional crystals.

Our findings will pave the way for the fabrication of functional micro-optical elements and integrated optical circuits.

Xiaosheng Liang

这是一片神奇的土地

This is a mysterious land

You will harvest (in Autumn) if you sow seeds (in Spring)

Ask and it will be given to you; seek and you will find;

knock and the door will be opened to you

Acknowledgements

Research Colleagues

Profs. K. Hirao, Drs. K. Miura, Y. Shimotsuma, S. Kanehira

(Kyoto University, Japan)

Profs. C. Zhu, My students and PostDoc researchers

(Zhejiang University and SIOM, CAS)

Prof. P. Kazansky **(Southampton Univ., UK)**

Dr. N. Jiang **(Arizona State Univ., UK)**

Thanks !

Compact femtosecond laser

Ultrashort-pulse laser

machining of dielectric materials

M. D. Perry et al., J. Appl. Phys., 85(1999)6803.

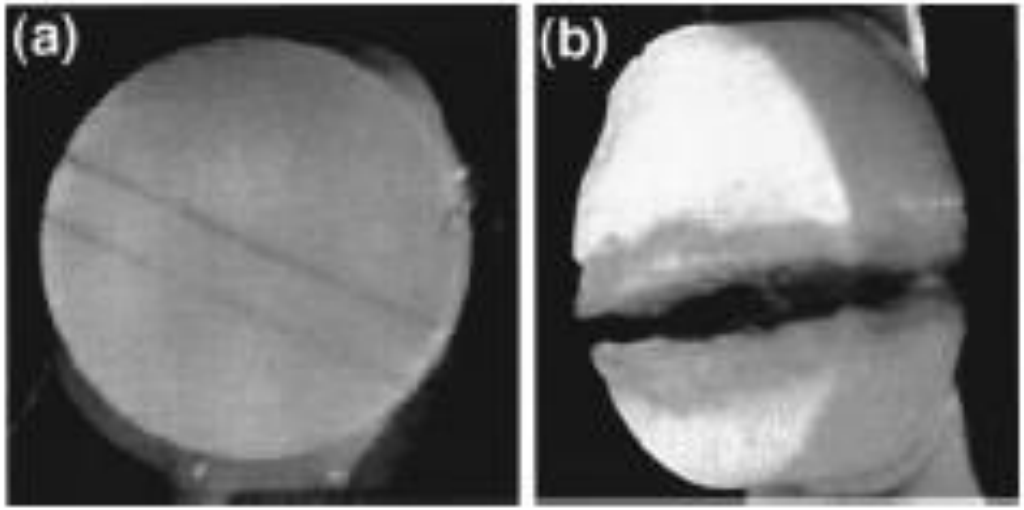
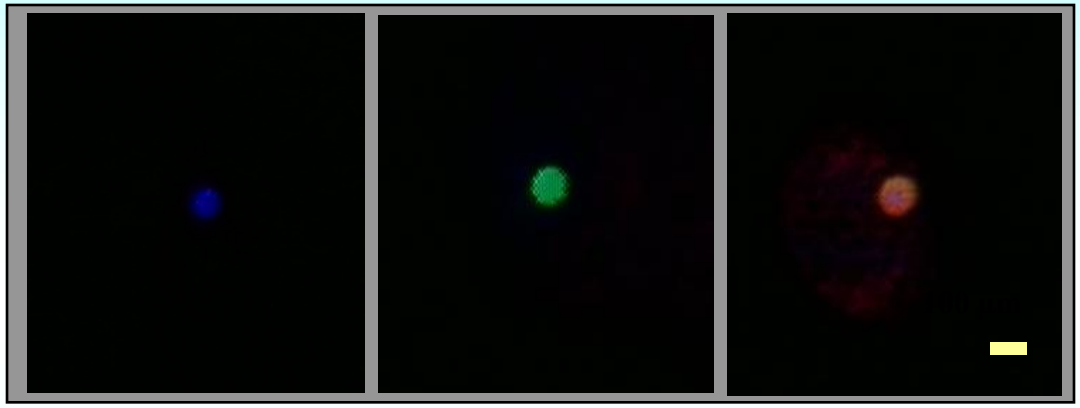
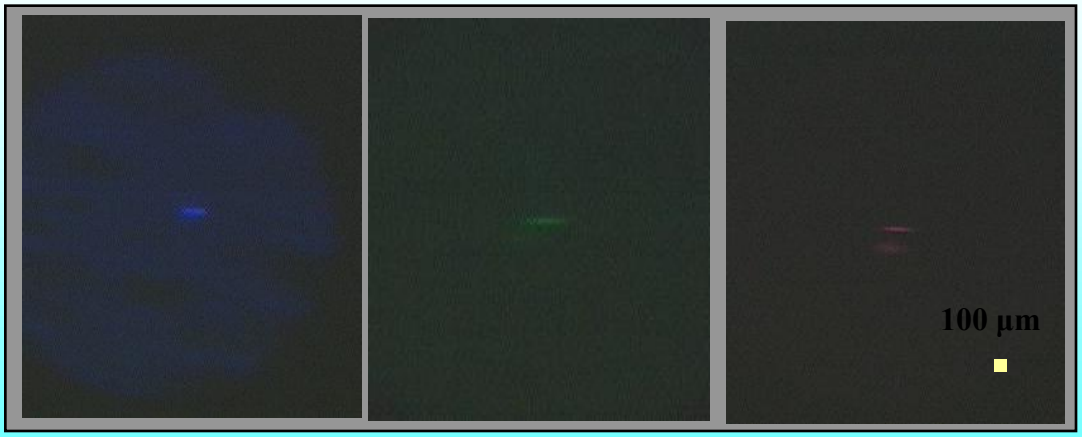


FIG. 10. Cuts in explosive pellet (LX-16-95% PETN) by a Ti:sapphire laser operating at 120 fs (a) and 600 ps (b). Thermal deposition in the long-pulse case caused the pellet to ignite and burn (b).

Space-selective emission in rare-earth-doped glasses excited by an 800nm femtosecond laser

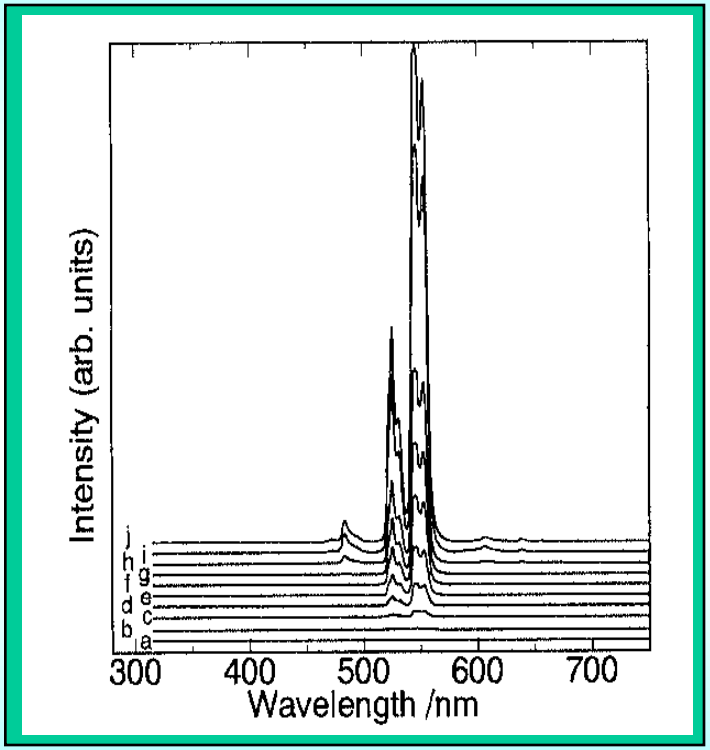


Front view

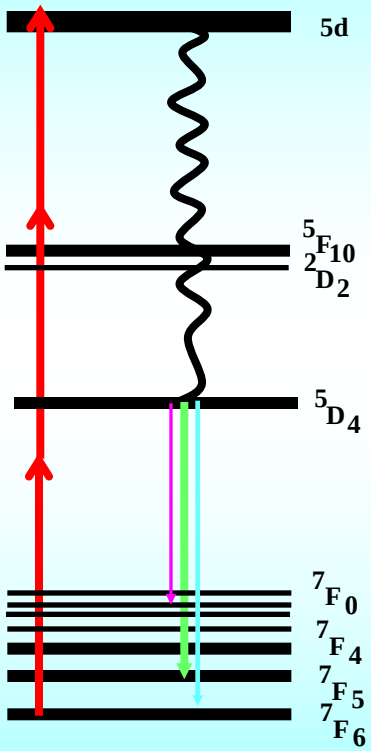


Side view

Emission spectra of rare-earth doped glass



Excitation power-dependence of the photoluminescence spectra of a Tb^{3+} -doped ZBLAN glass



Energy levels of Tb^{3+}

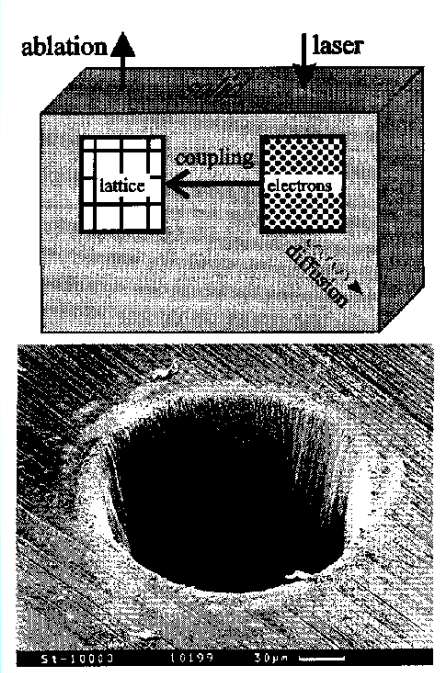
Precise surface processing

$L_D=(D\tau)^{1/2}$

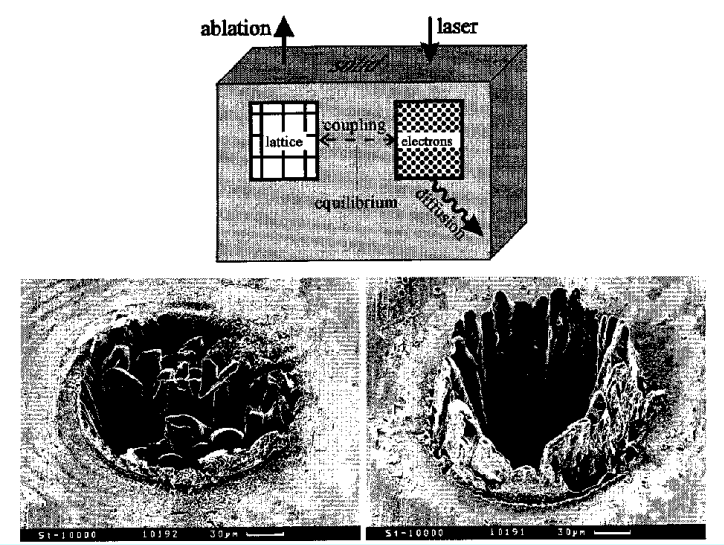
$D=k_T / \rho C_p$

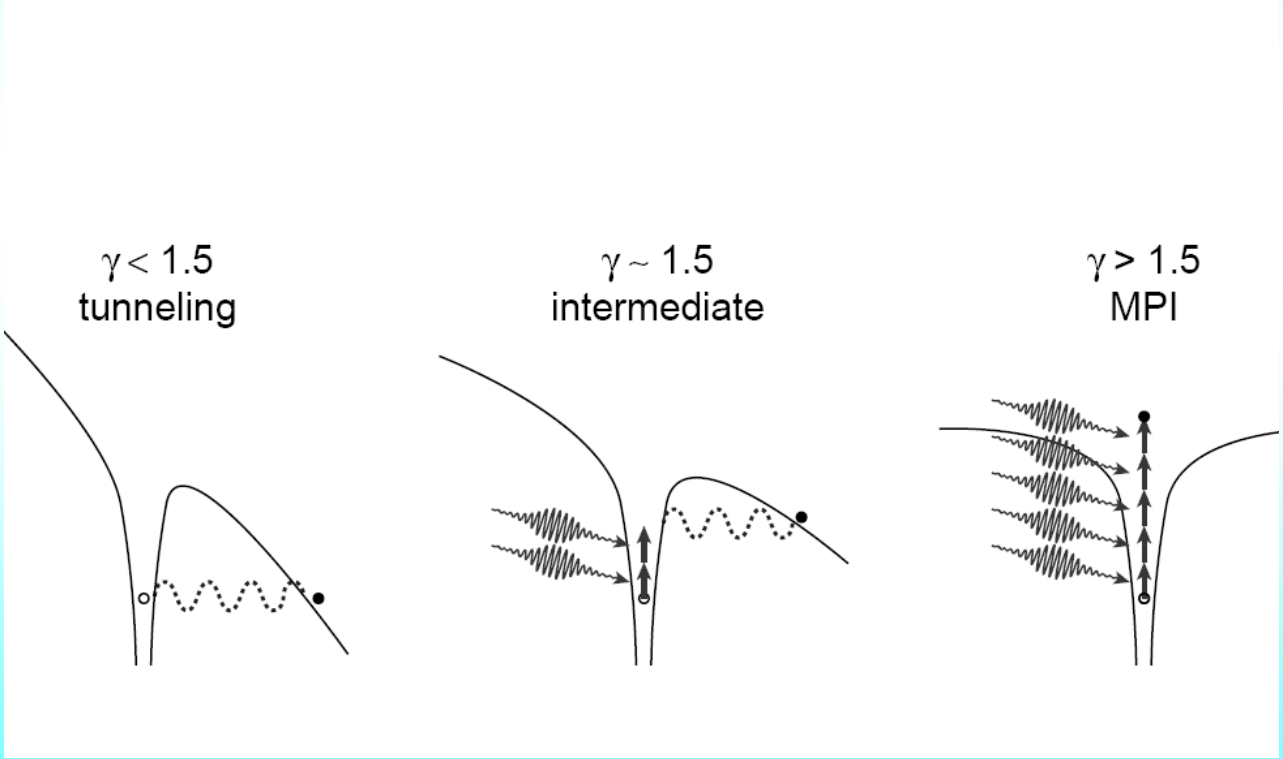
(1ps, 10nm)

B. N. Chichkov et al., Appl. Phys. A63 (1996) 109.



a hole drilled in steel with 200fs laser pulses at 780nm



holes drilled in steel with 80ps(left)and 3.3ns(right) laser pulses at 780nm

$$\gamma = \frac{\omega}{e}\left[\frac{m c n \varepsilon_0 E_g}{I}\right]^{1/2}$$