Advanced Topics on Highly Sophisticated Materials
（物性制御学特論）

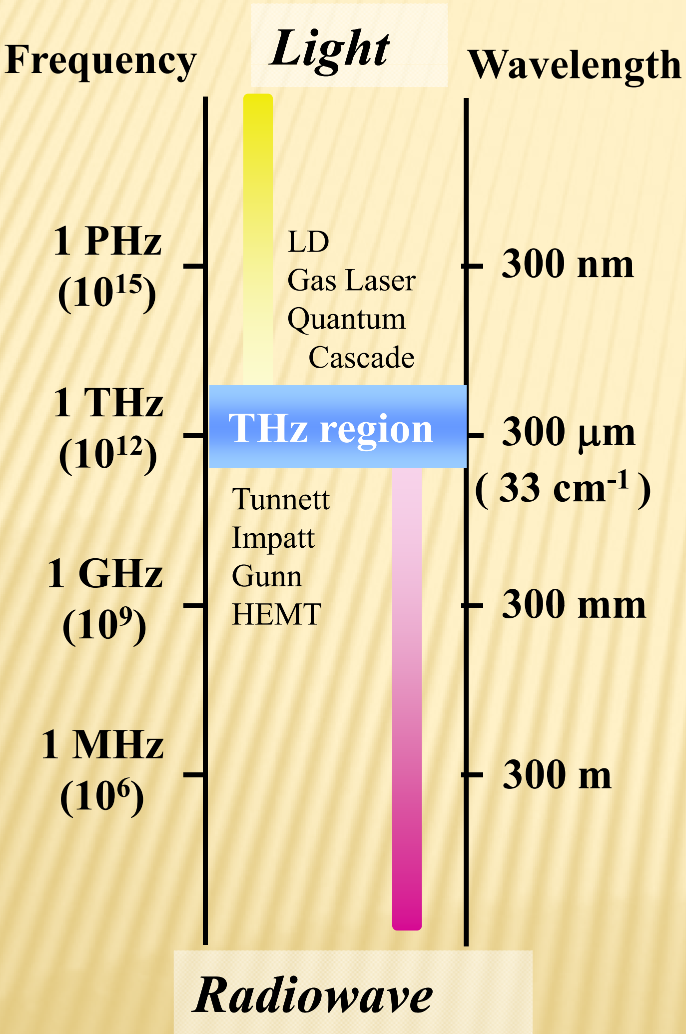
- Coherent THz wave generation and its application for biomedical and structural defects -

Yutaka Oyama

Dep. MS&E, Graduate School of Eng. Tohoku Univ. ,Sendai, Japan

oyama@material.tohoku.ac.jp

Background & Motivations



THz region（far-infrared region)

- 0.1-10 THz, 3 mm-30 μm
- between millimetre waves and infrared
- vibrational modes in macro-molecule

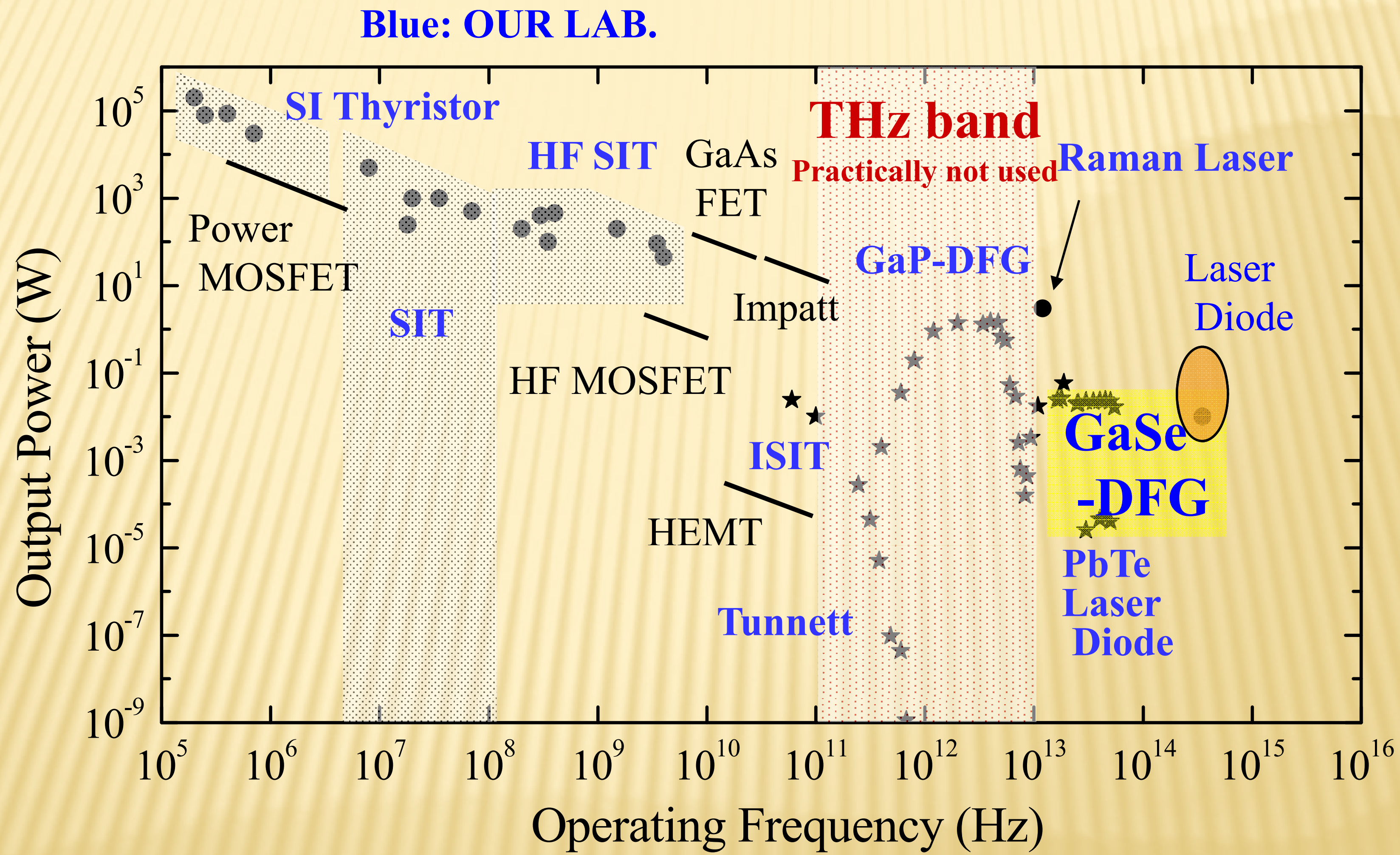
Applications

- spectral measurement (**fingerprint**) and imaging of macro-molecules (*e.g.*, DNA)
- detection and treatment of cancer tissue (**bio medical**)
- Harmless & non destructive inspection
- Security

etc.

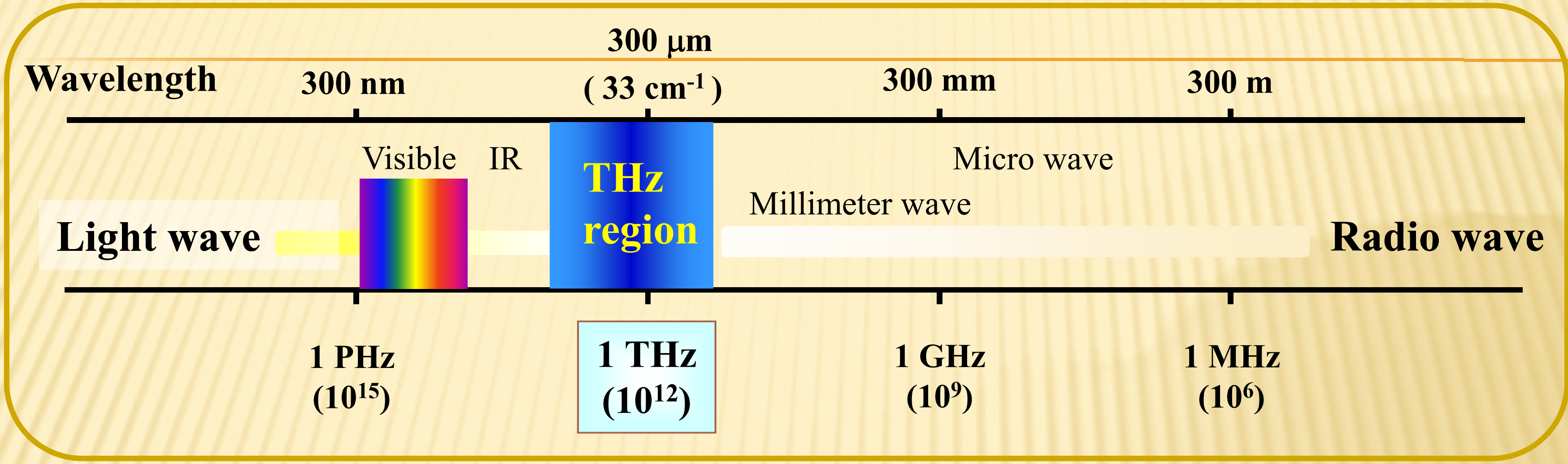
Very wide variety of important applications

RADIO WAVE & LIGHT SOURCES DEVELOPED



"Whole the frequency must be used for communication in future"
by Prof. Hidetsugu Yagi (1886-1976: Inventor of Directive Short Wave (Yagi) Antenna)
Tohoku, Osaka Univ.

THz wave and its application



Characteristics and functions of our THz source (GaP)

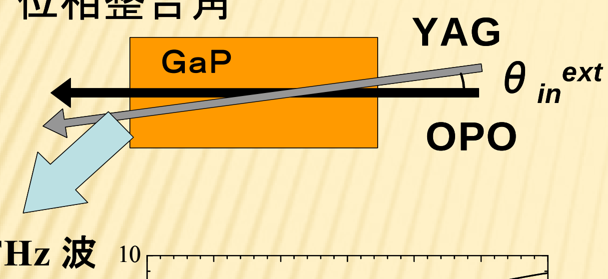
- **High power ~1.5W(max) coherent source**
- **Wide frequency tunable (0.1-7THz)**
- **High purity /coherent source (Δf~0.1GHz)**
- **Compact source (1m x 1m: ➡ 0.3m x 0.3m)**
- **Full automated**

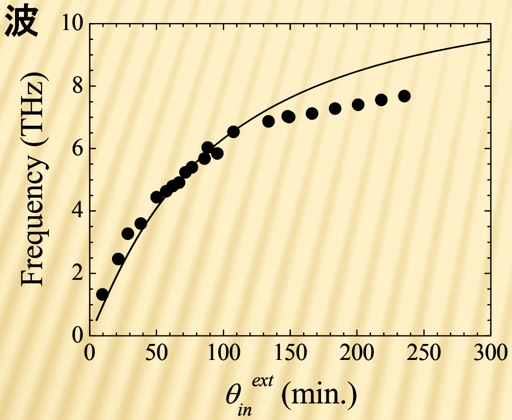
Application of THz wave

- **Bio-medical**
- **Nondestructive inspection (Harmless)**
- **Security**
- **High speed THz communication**

THz wave generation from bulk GaP

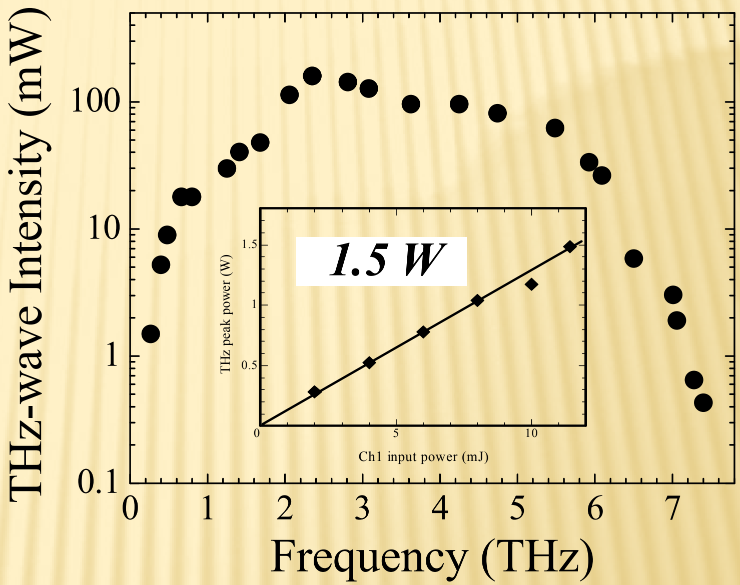
Differential Frequency Generation





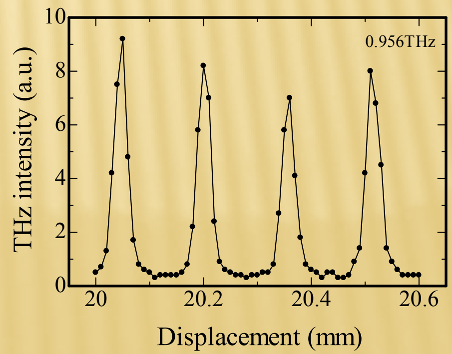
入射光周波数と θ_{in}^{ext} の調節
↓
周波数変調が可能

Widely frequency tunable source (0.2～7.5 THz, 1.5W)



Narrow line width

500 MHz
(0.015 cm^{-1})



GaP DFG, FTIR and TDS (time domain spectroscopy)

FTIR ***white light source***

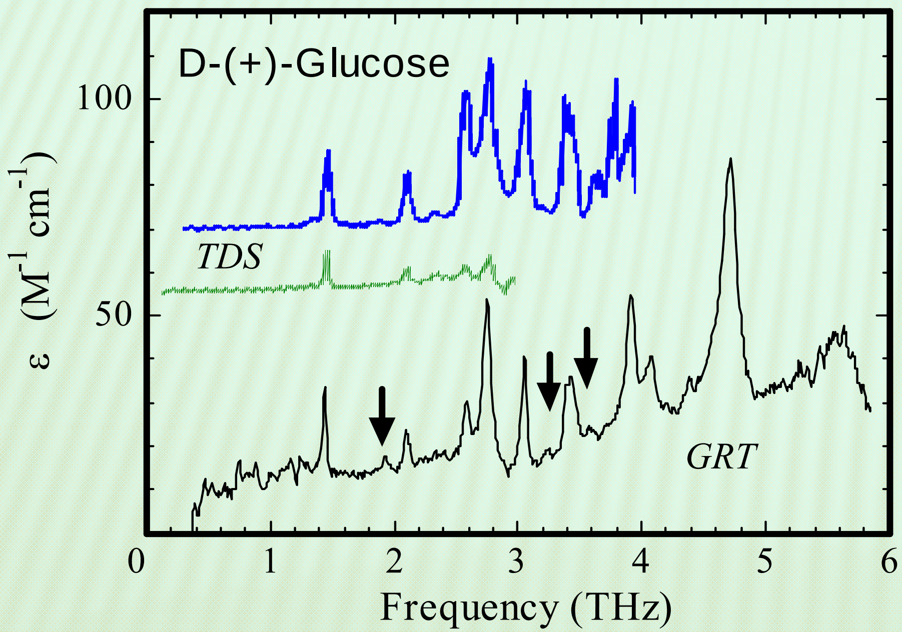
TDS ***white light source (femto sec. laser)***

||

From time domain to frequency domain

By Fourier transform

⇔ ***GaP DFG = monochromatic frequency tunable source***



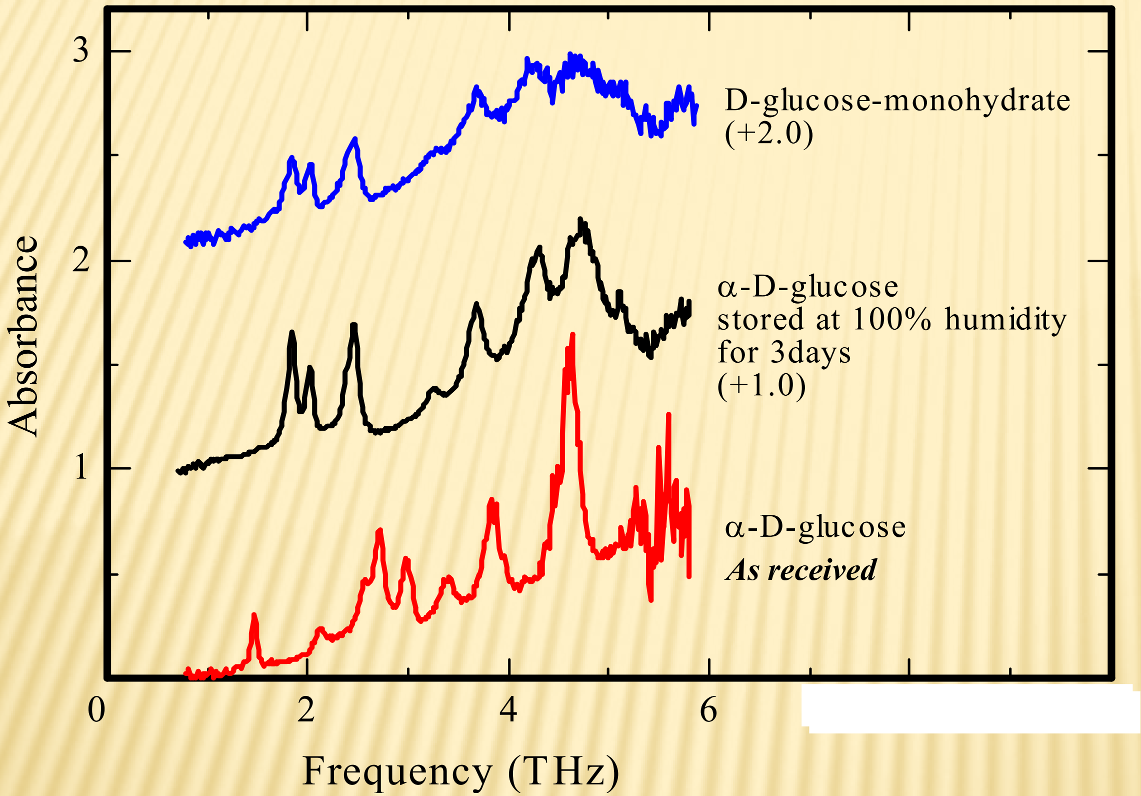
Direct reading of resonance frequency

⬇

Precise determination of resonance frequency

THz spectra of glucose (by Cr:F-source system)

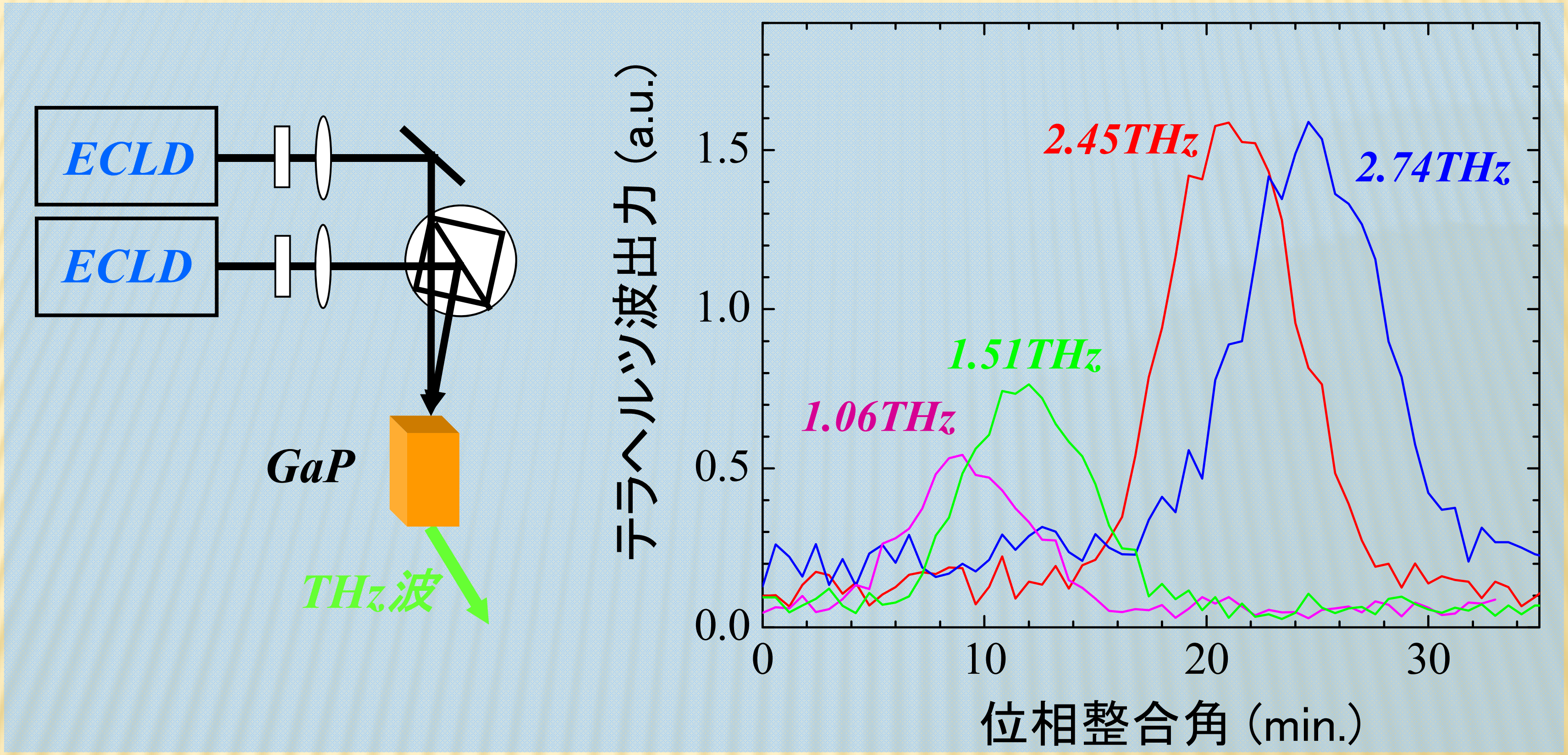
The effects of hydration (hydrogen bonding)



α-D-glucose has changed to monohydrate stored in normal atmosphere

The reaction is reversible by drying in vacuum

CW THz wave generation by LD



LD (laser diode) excited CW THz wave

Ultra narrow line width THz light

DEVELOPMENT OF THz SOURCES

THz wave generation

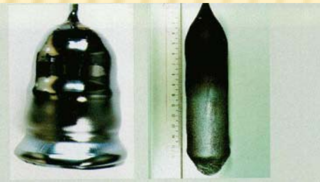
An approach from light wave

Application of phonon-plariton in semiconductor crystal

proposal 1963 J.Nishizawa

Difference-frequency generation (DFG) using near-infrared light

realized 1983 J.Nishizawa & K.Suto



GaAs crystal

GaP crystal

Semiconductor crystals for THz generation (by NLO crystals)

- GaAs
- GaP
- **GaSe**

GaSe crystal

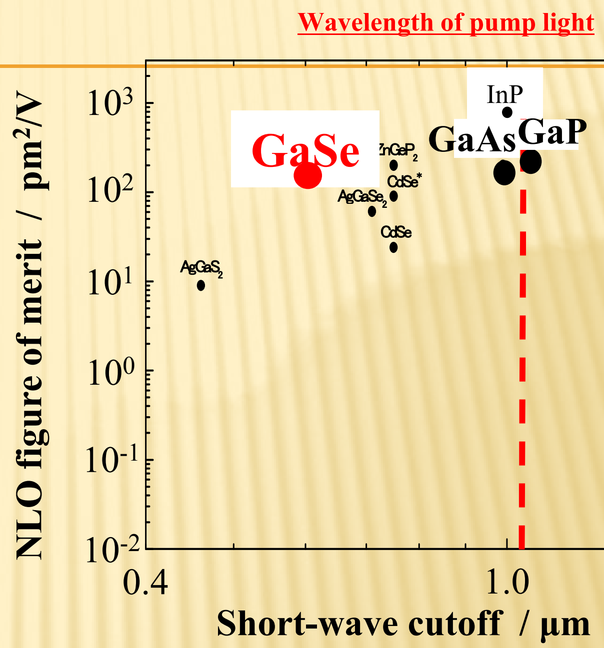
High power, coherent and wide frequency tunable THz wave generation

Nonlinear optical (NLO) crystals

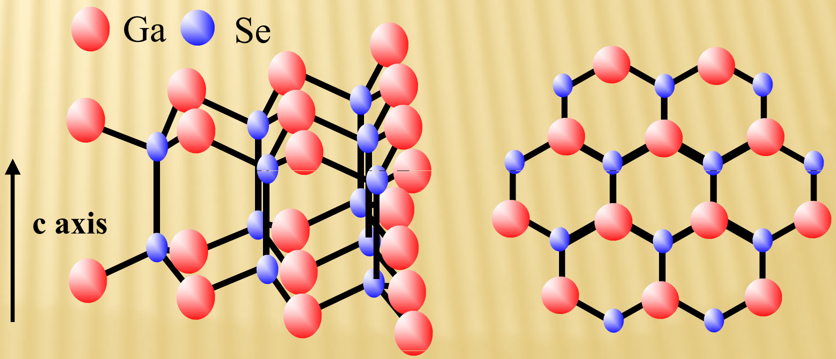
Merit of GaSe

- **Cut off wavelength(0.62μm)**
  - ➡ Transparent in infrared and THz region
- **High 2nd -order nonlinear optical coefficient**
  - ➡ d_{22}= 128pm^2/V at 0.62μm
- **Layered structure in the c-axis direction**
  - ➡ Collinear phase matched DFG Due to its birefringence
  - ➡ Construction of compact THz-wave generation system
- **THz-wave generation in super wide frequency range (~110THz)**

Wei Shi and Yujie J.Din
Proceeding of Conference on Lasers and Electro-optics(CLEO : 2003)



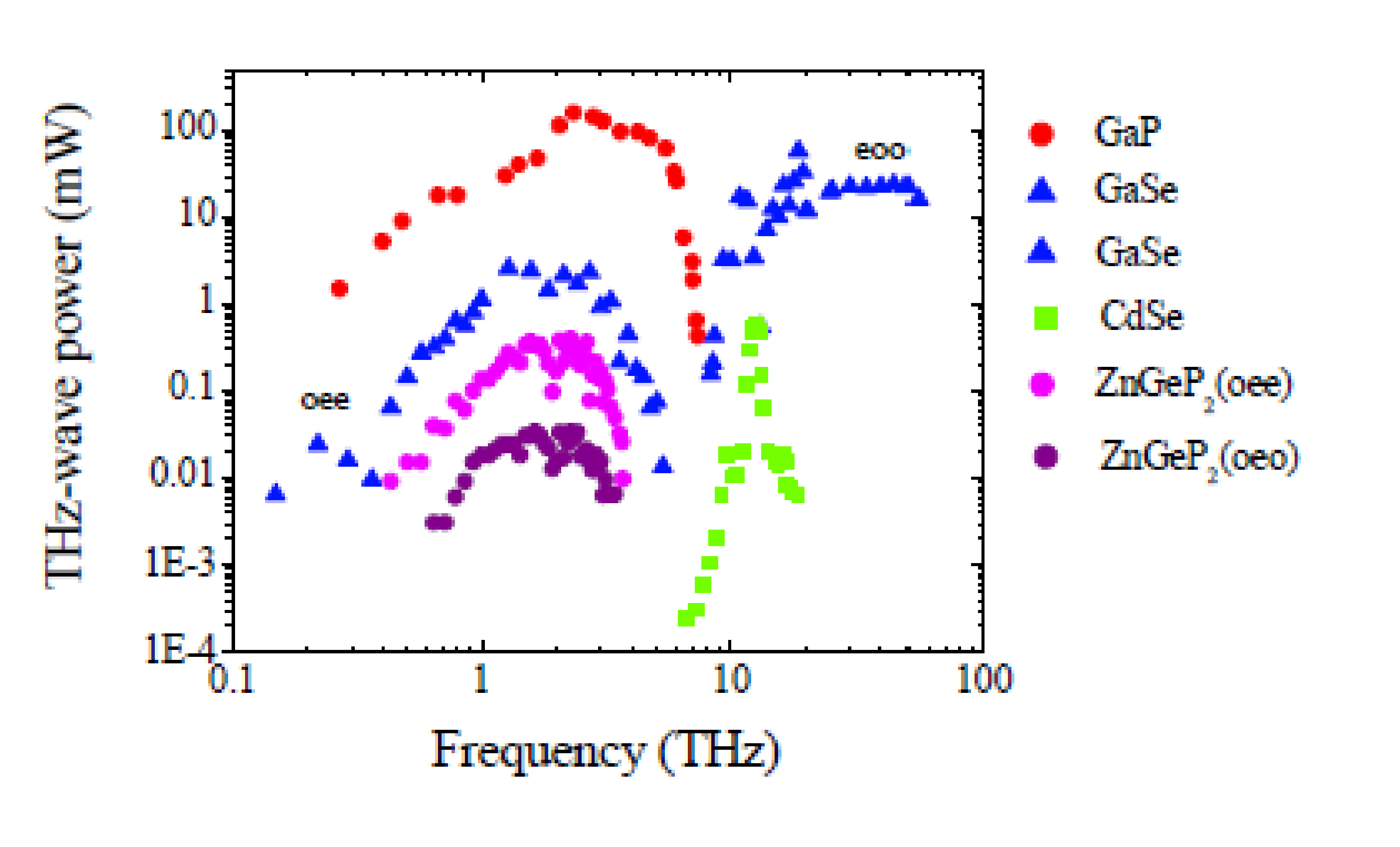
K. L. Vodopyanov
J. Opt. Soc. Am. B 16 (1999) 1579.



(a) (100) direction (b) (001) direction

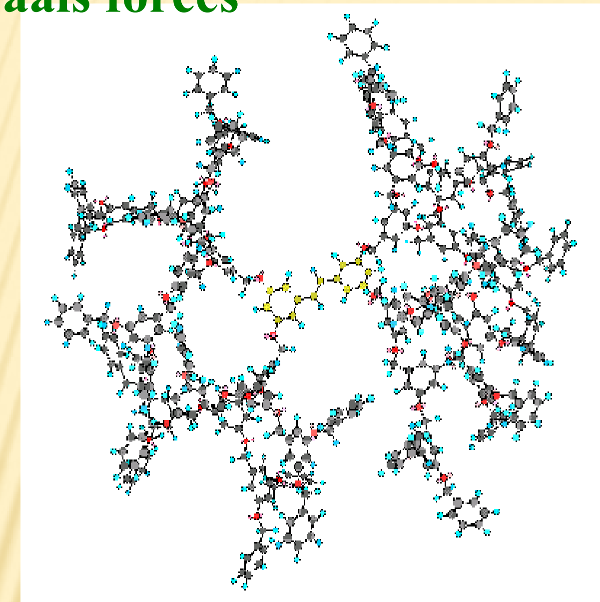
Unit cell of GaSe crystal

THz generation from various semiconductor crystals

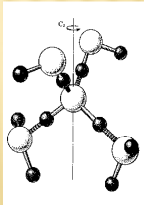


Vibration of organic molecules

Inter-molecular interaction
- hydrogen bonding
- van der Waals forces



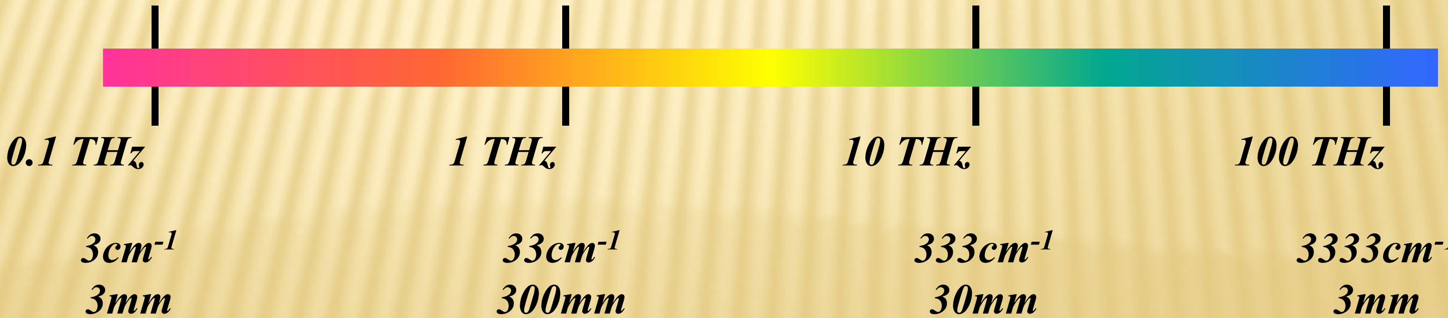
local vibrations



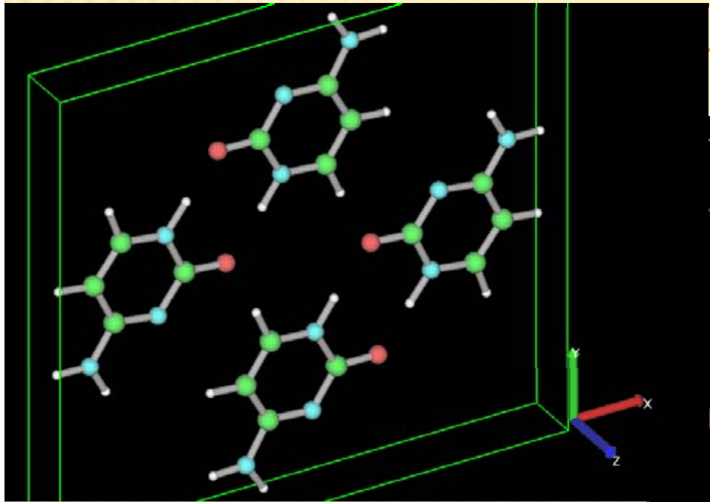
Bio-medical Application

Non destructive inspection

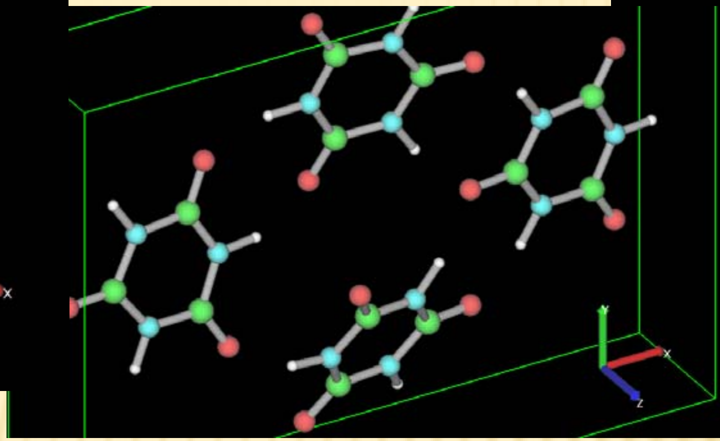
hν~
Room temp.
Human body temp.



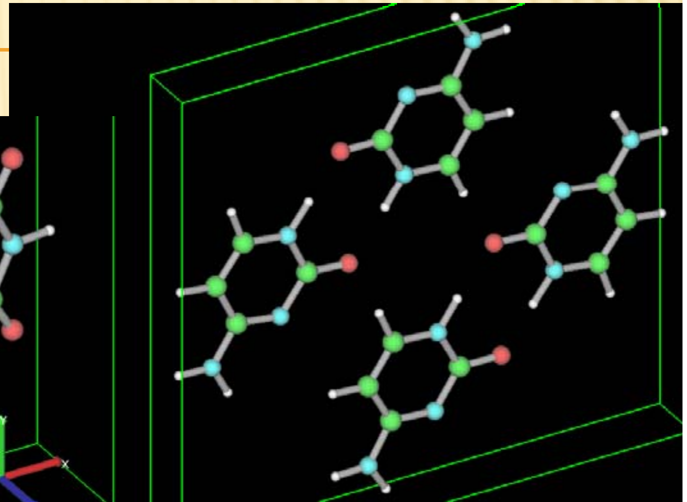
THz vibration modes （Gaussian03）



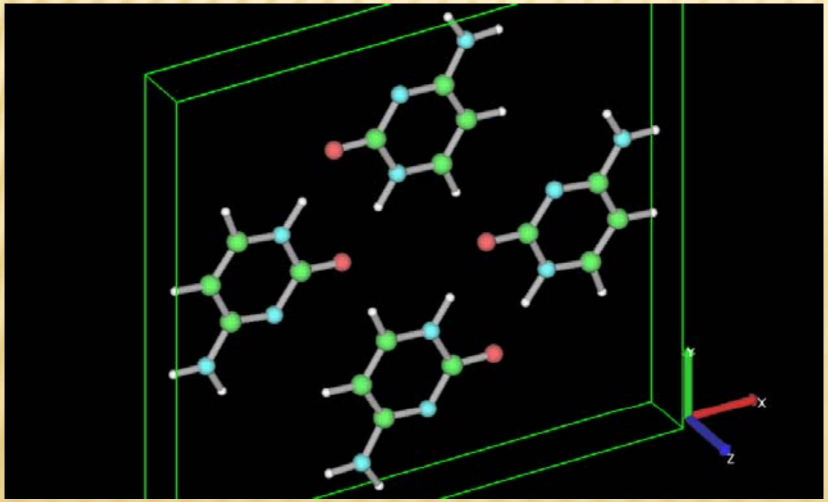
In-plane



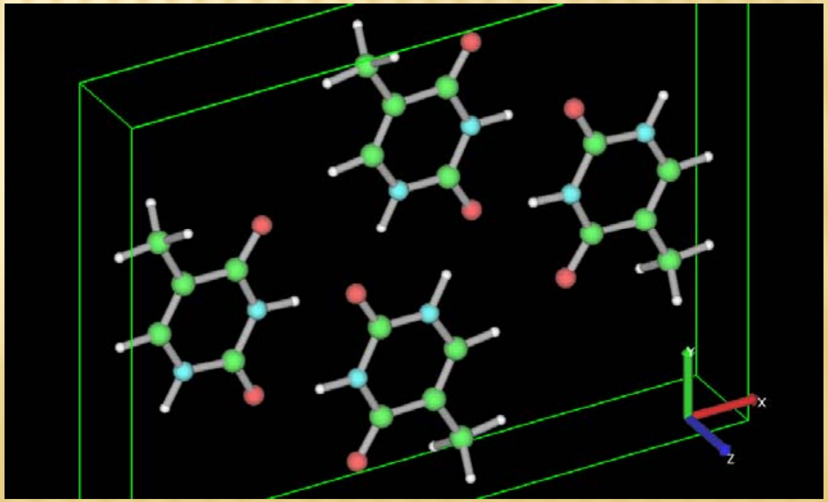
In-plane + out of plane



Out of plane

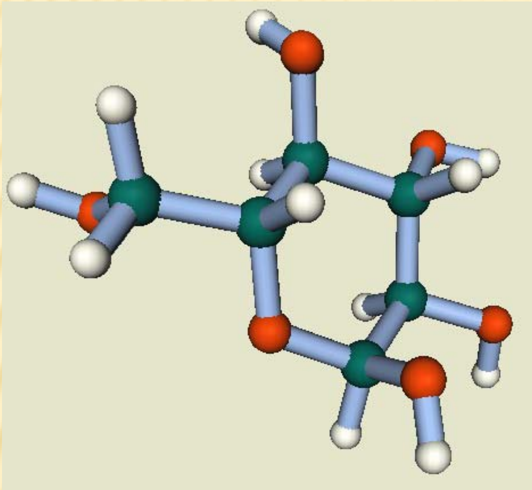


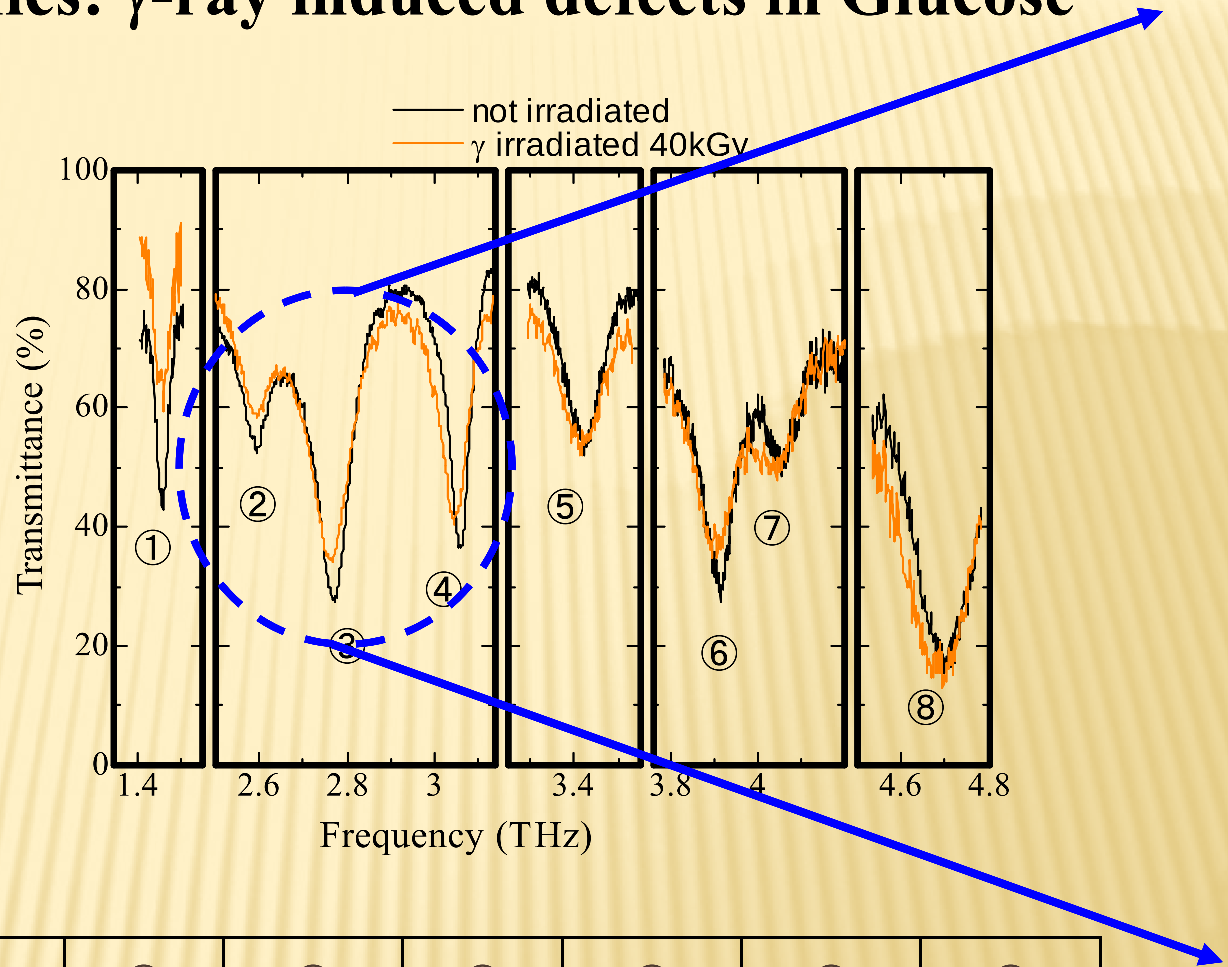
translation



Localized vibration

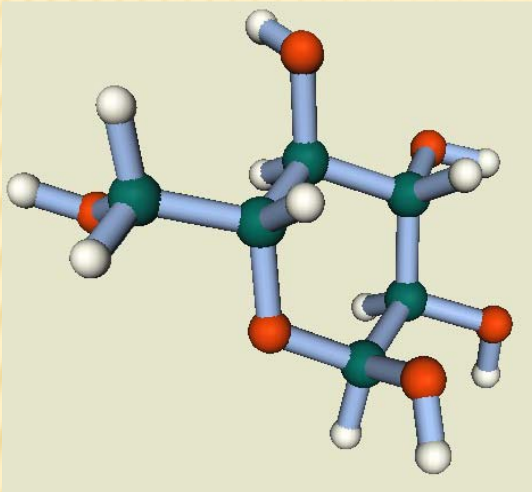
Defects in organics: γ-ray induced defects in Glucose

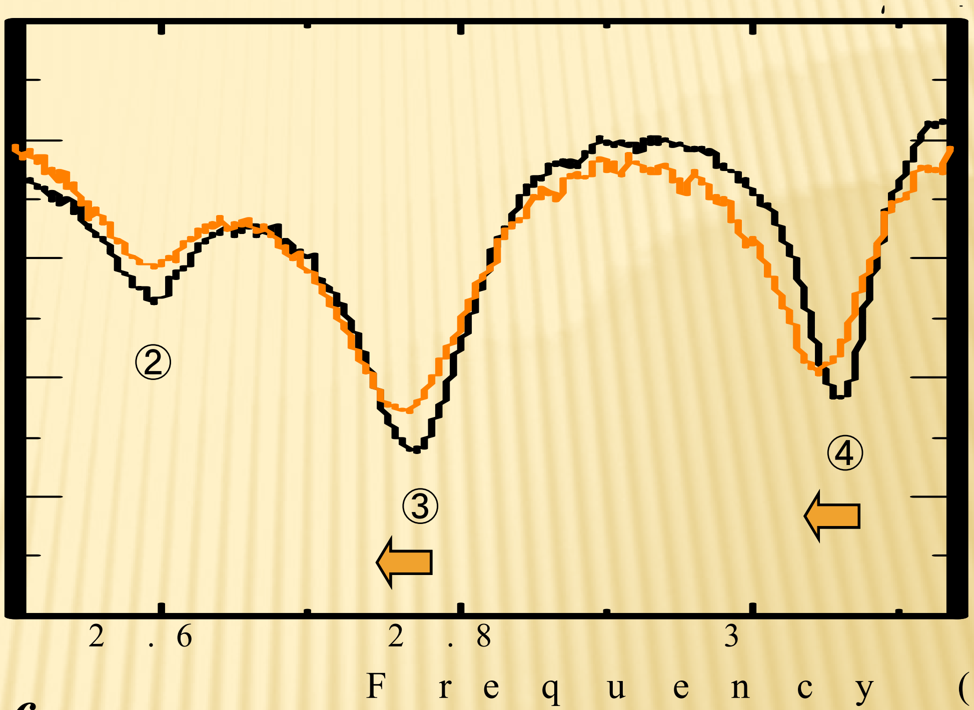




	①	②	③	④	⑤	⑥	⑦	⑧
Not irradiated	1.455	2.595	2.772	3.060	3.419	3.915	4.052	4.698
γ-ray irradiated	1.455	2.590	2.763	3.043	3.414	3.902	4.032	4.687
frequency shift	0	-5GHz	-9GHz	-17GHz	-5GHz	-13GHz	-20GHz	-11GHz

γ-ray induced defects in Glucose





Inter molecular defects

Lower resonance vibration frequency

	①	②	③	④	⑤	⑥	⑦	⑧
Not irradiated	1.455	2.595	2.772	3.060	3.419	3.915	4.052	4.698
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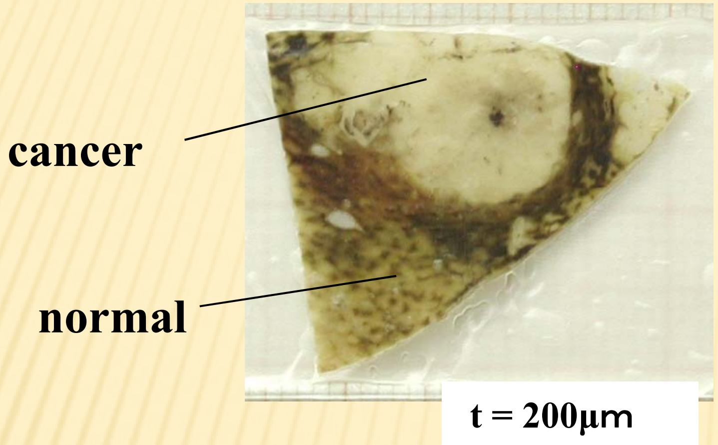
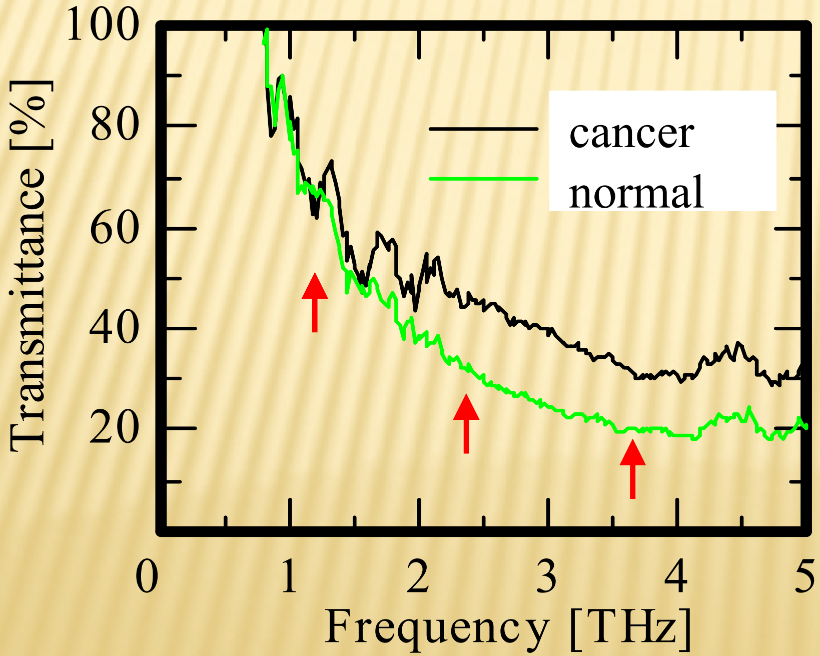
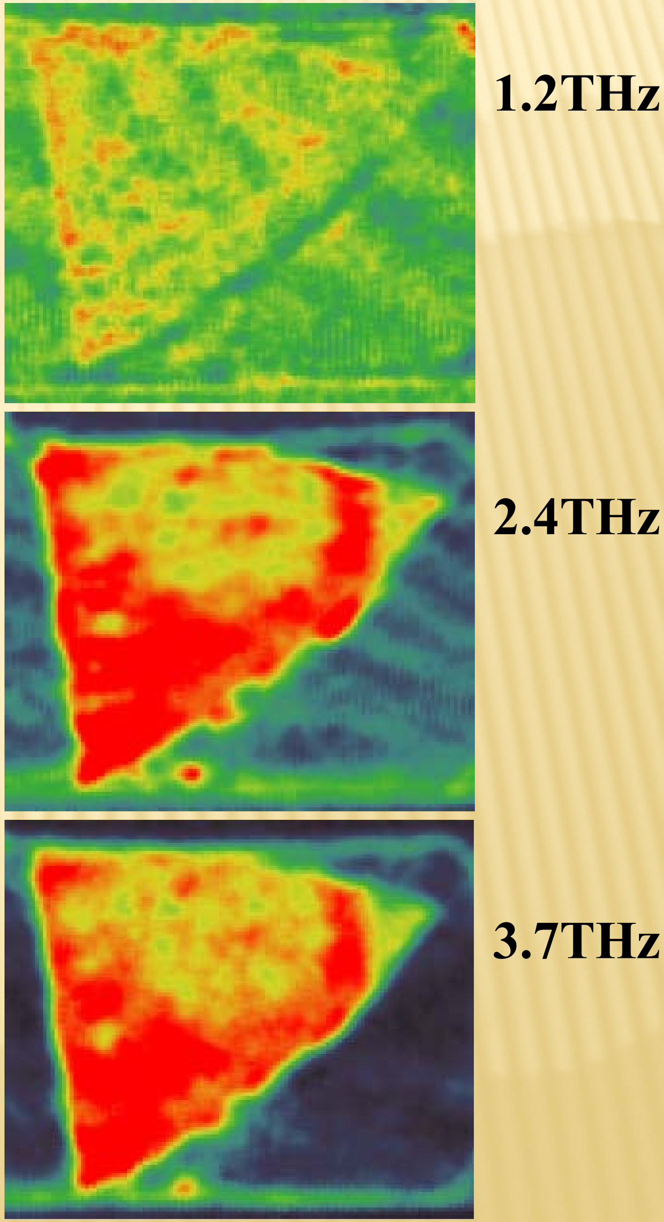
THz spectral imaging of liver cancer tissue

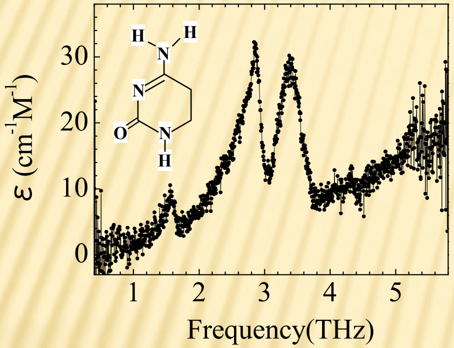




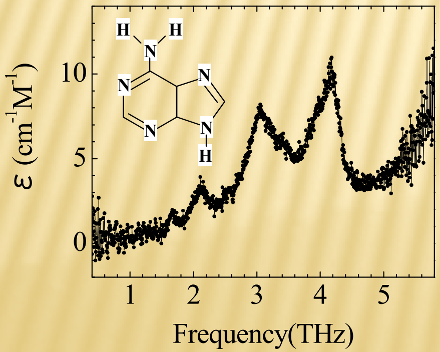


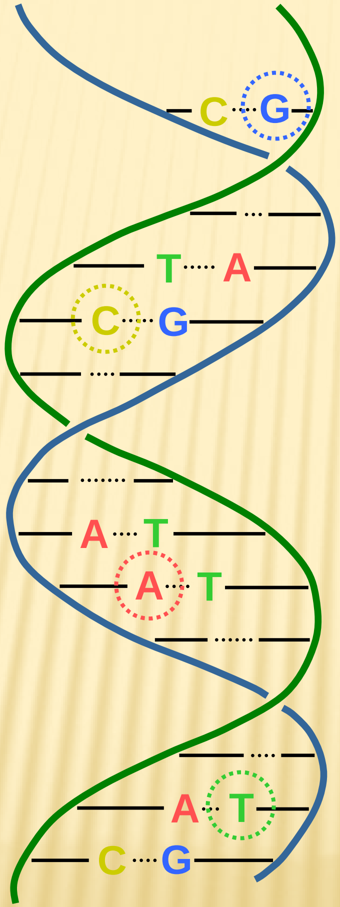
THz spectra of DNA/RNA bases

C（cytosine）

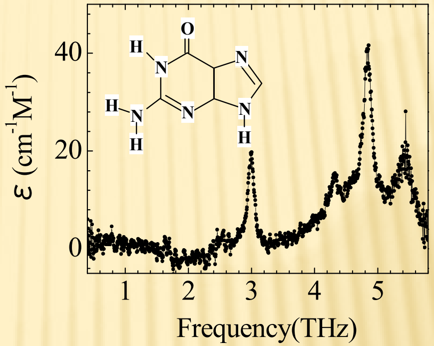


A（adenine）

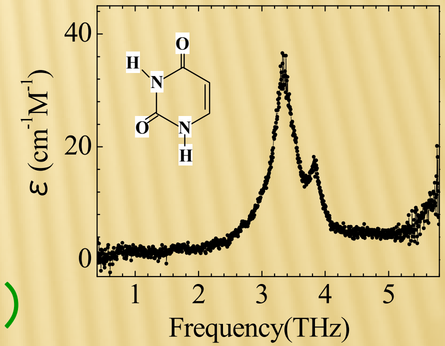




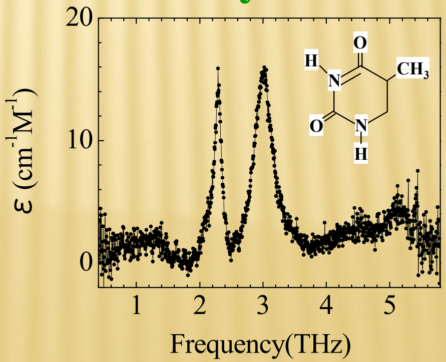
G（guanine）



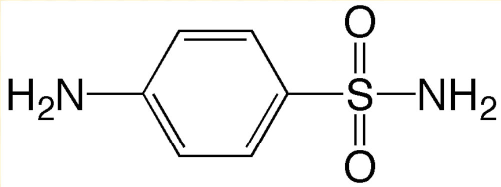
U（uracil）



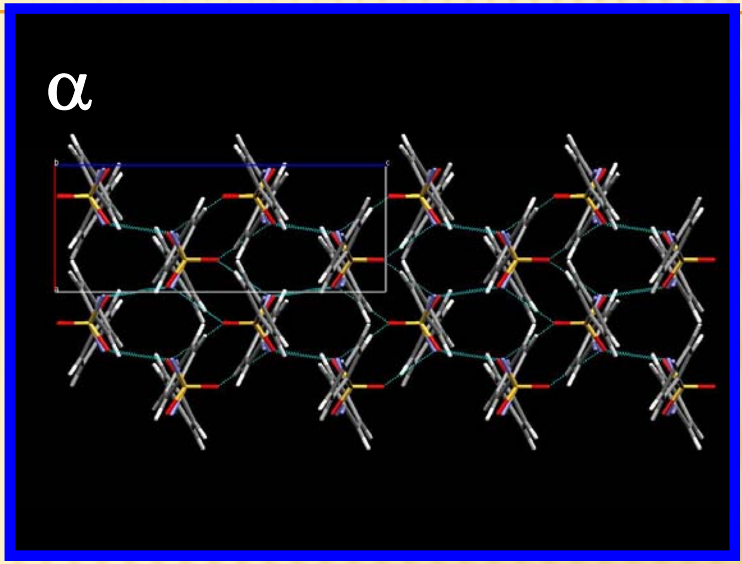
T（thymine）



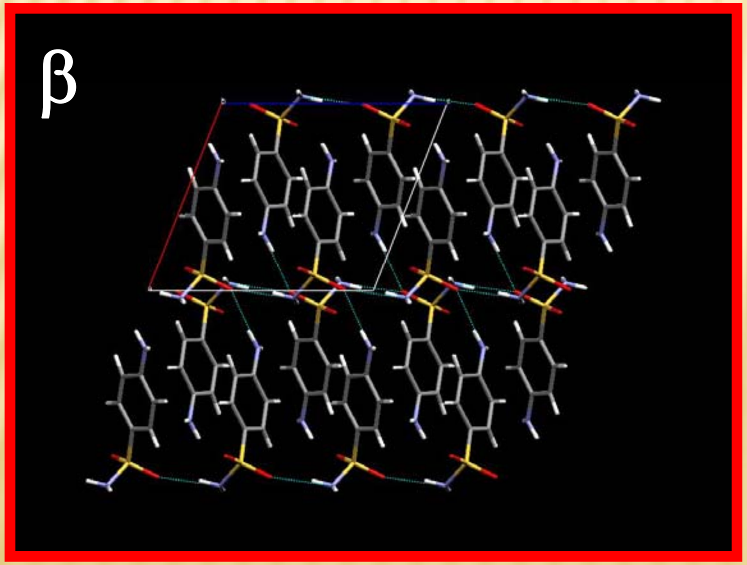
Crystal Structures of Sulfanilamide: Views from b Axes



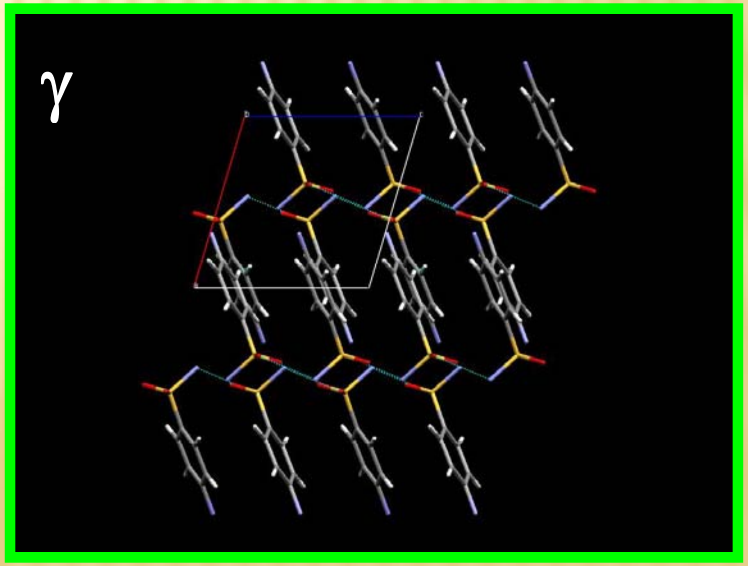
α



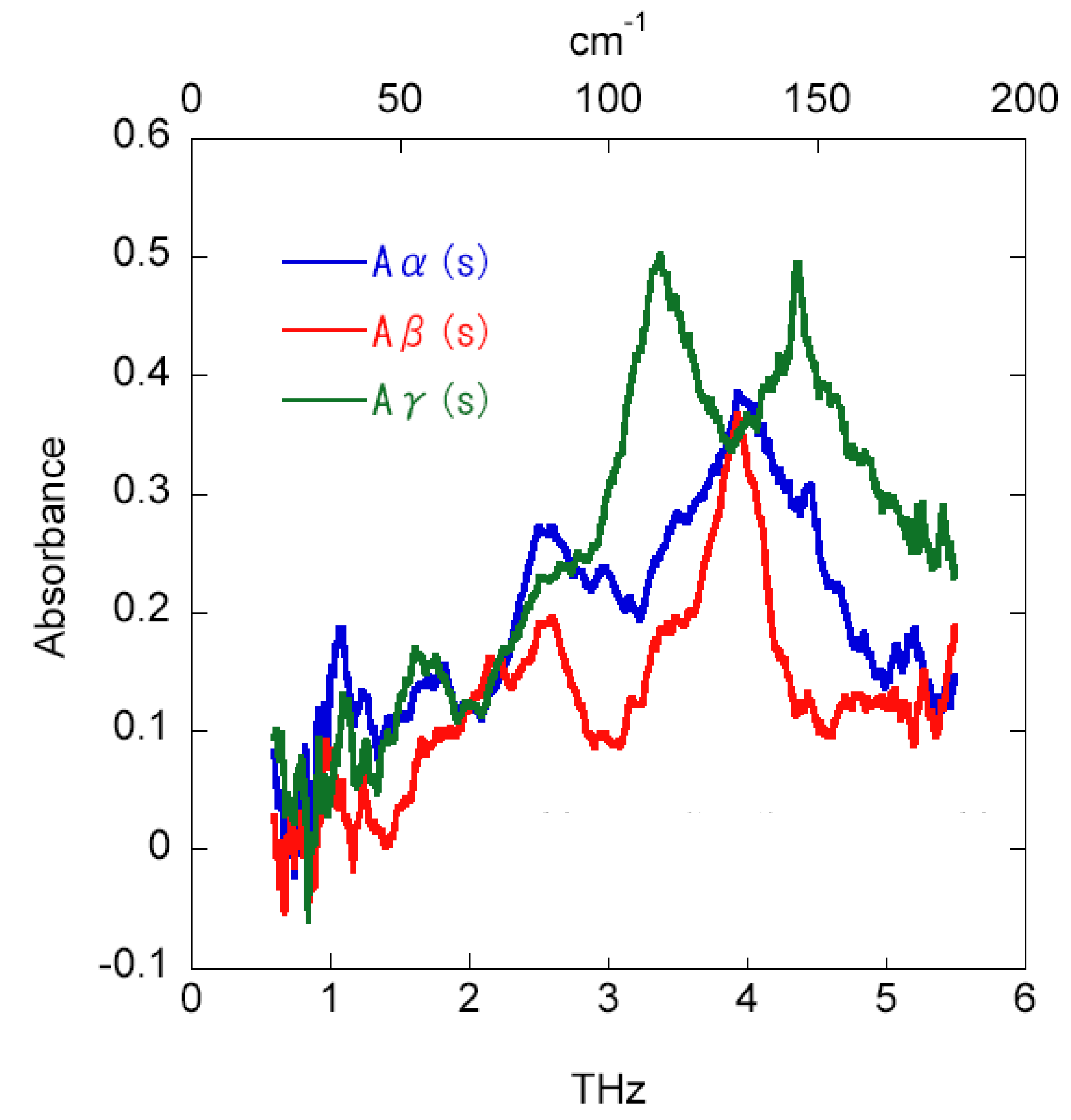
β

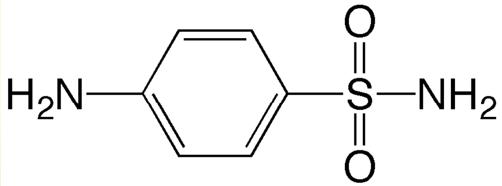


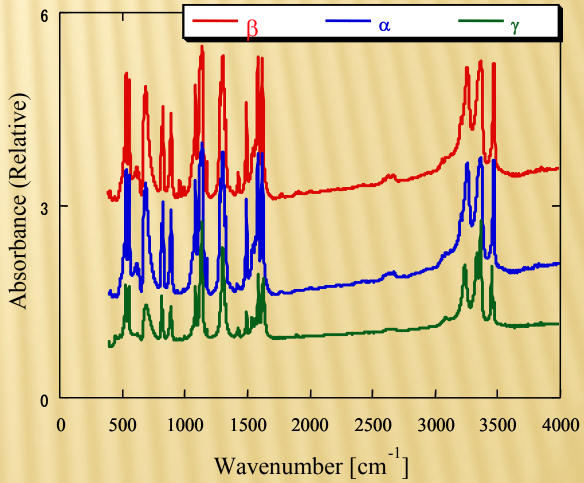
γ



Terahertz Absorption Spectra of Sulfanilamide: Polymorphic forms of medicines

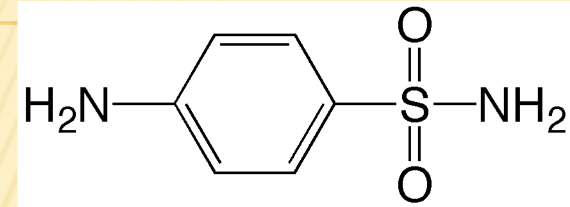






FTIR(Mid-IR)
NO difference

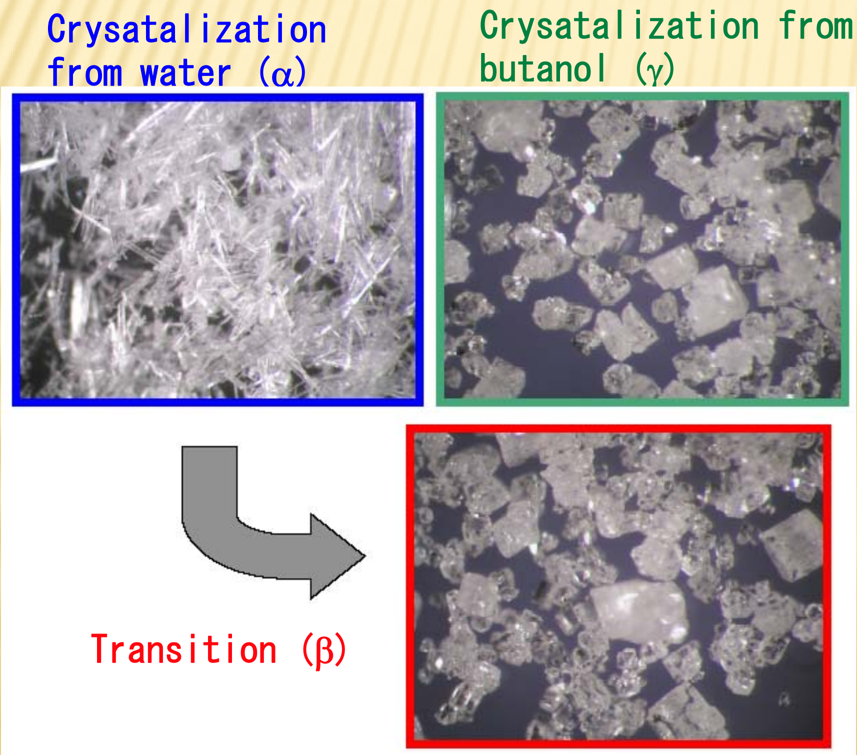
The Different Polymorphic Forms of Sulfanilamide



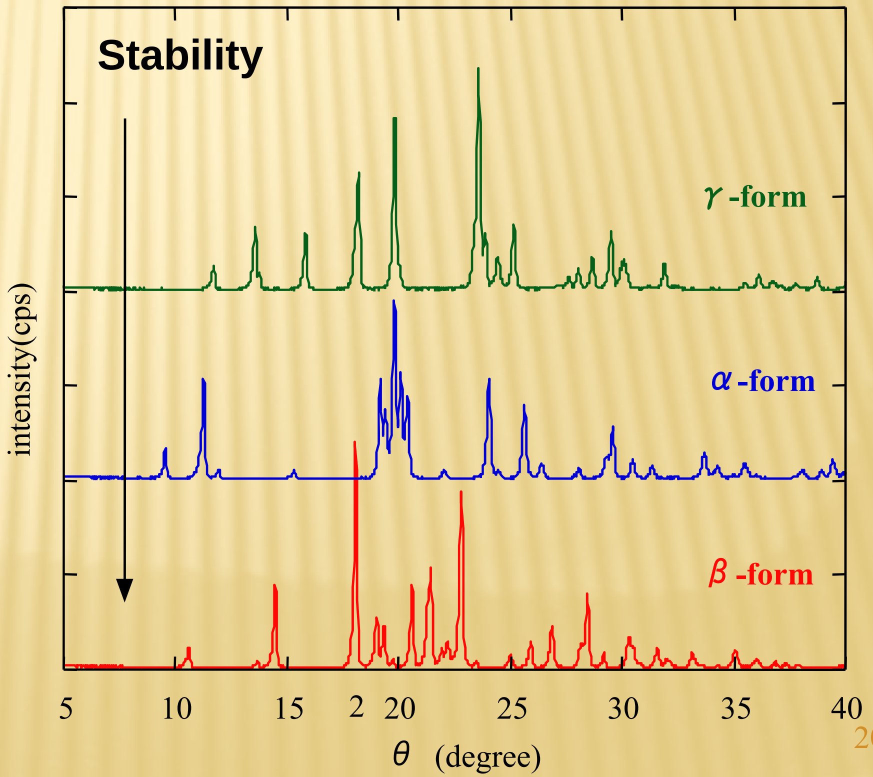
Sulfanilamide is known to exist in three polymorphic crystalline forms.

Thermodynamic Stability: $\gamma < \alpha < \beta$

Crystal forms of sulfanilamide

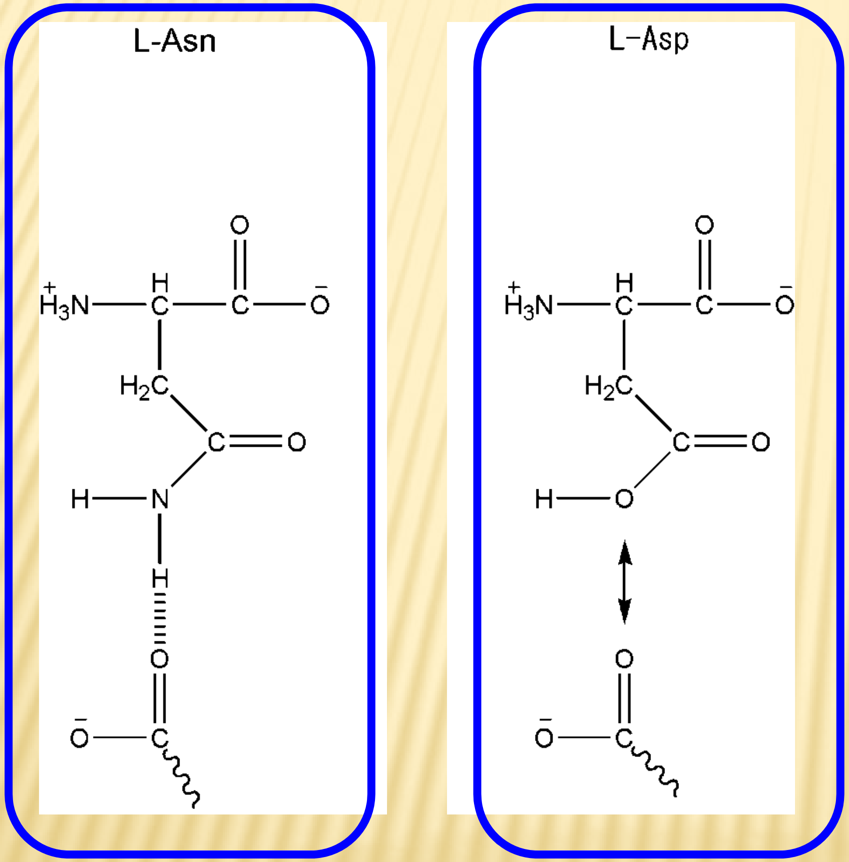


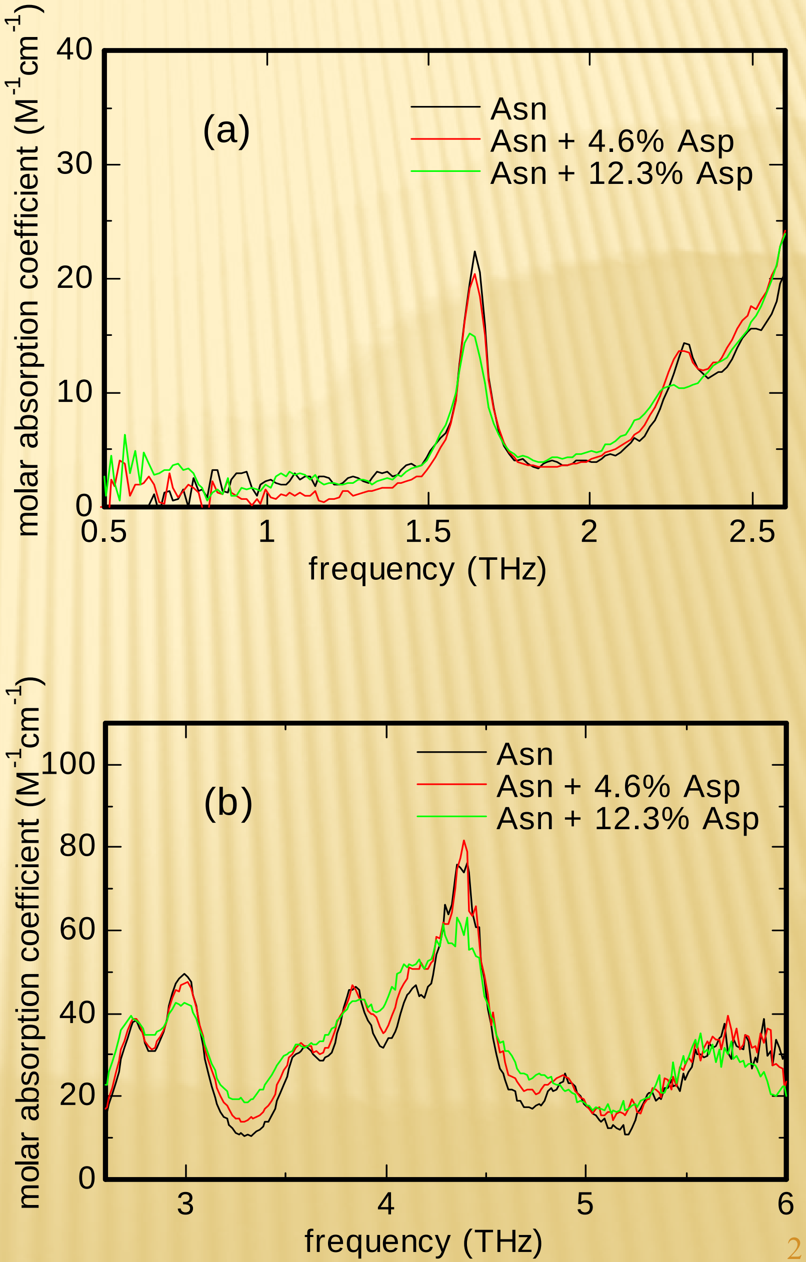
XRD spectra



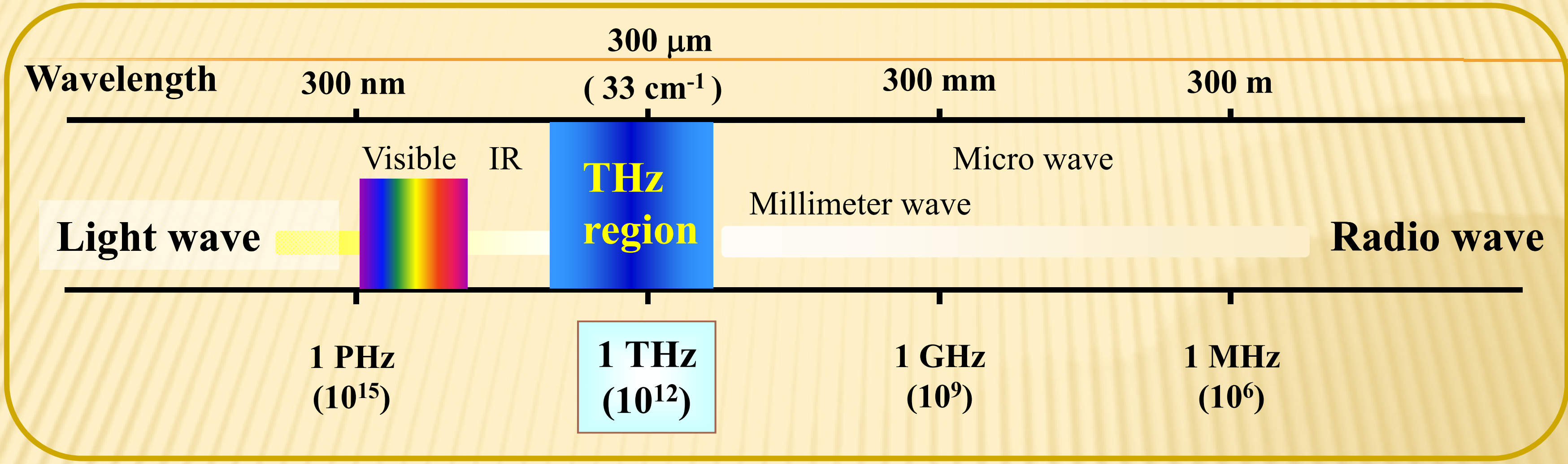
THz spectra of L-asparagine-L-aspartic acid solid solution

Medical application
Placebo
PAT(process analytical tool)





THz wave and its application



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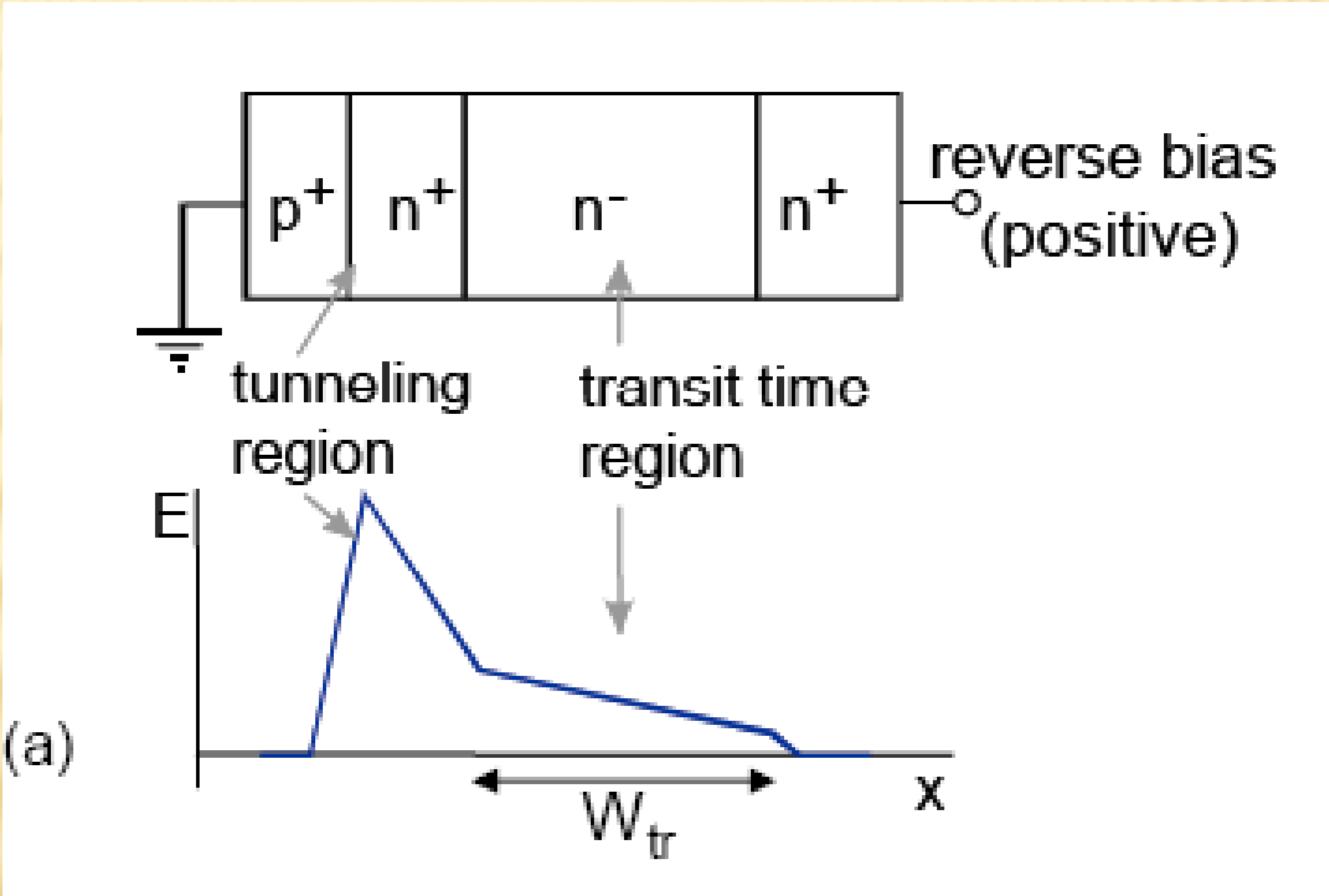
- **High purity /coherent source (Δf~0.1GHz)**
- **Compact source (1m x 1m: → 0.3m x 0.3m)**
- **Full automated**

Application of THz wave

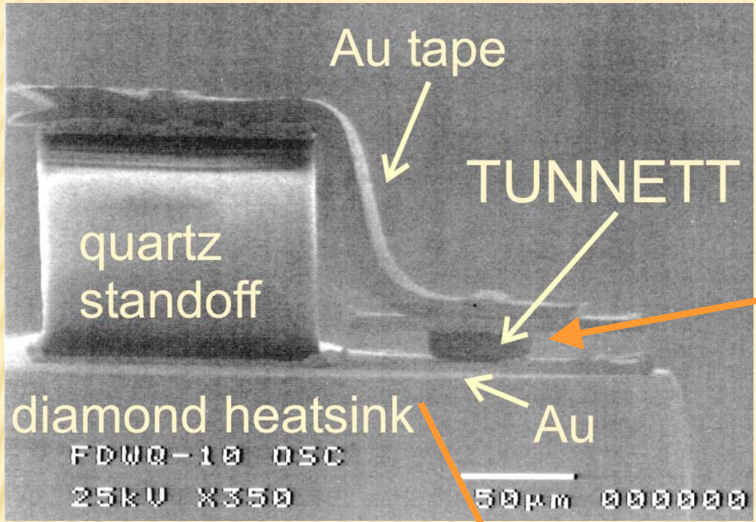
- **Bio-medical**
- **Security**
- **Nondestructive inspection (Harmless)**
- **High speed THz communication**

OPERATION PRINCIPLE OF MM-WAVE TUNNETT

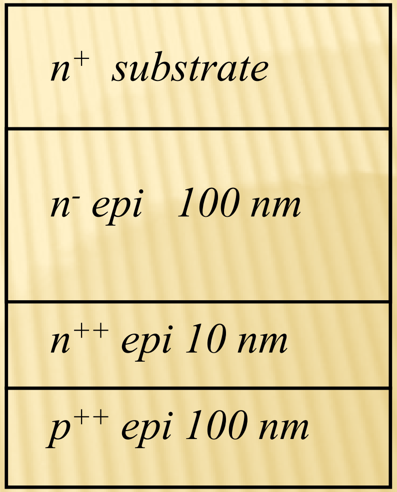


Invented by Prof. J-I Nishizawa

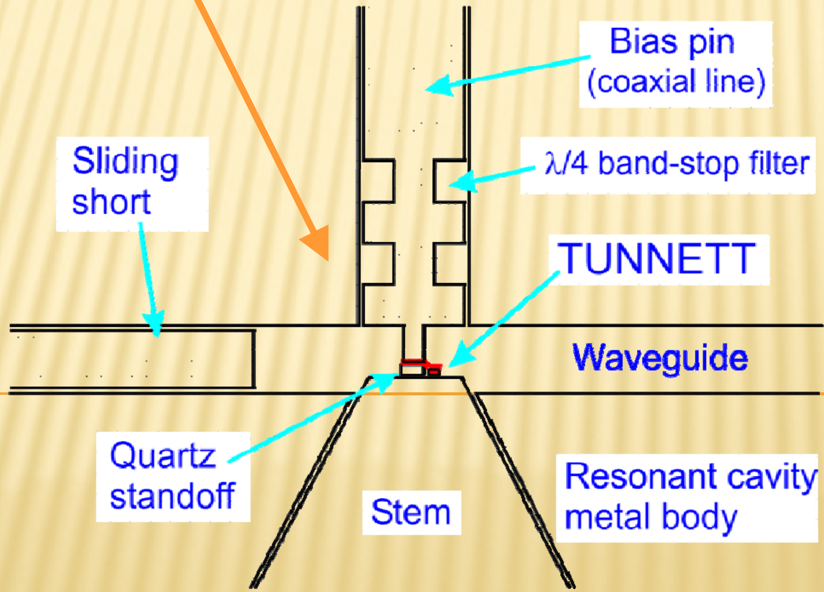
Device assembly of TUNNETT oscillator



Resonant cavity

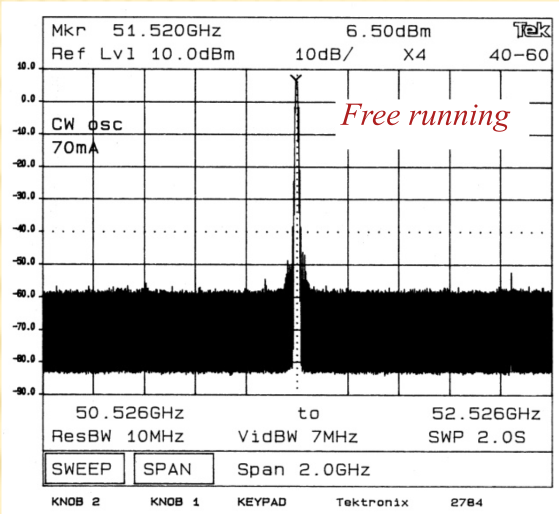


Layered structure of TUNNETT chip

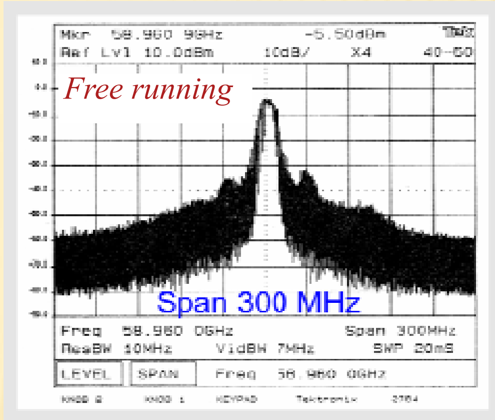


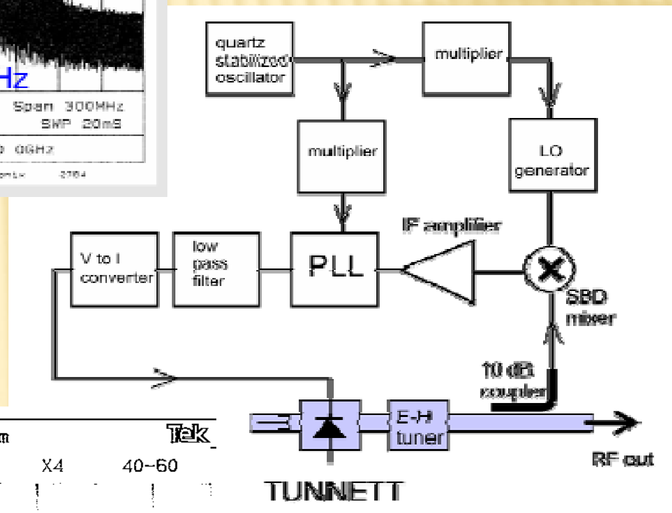
Cavity structure

Oscillation characteristics of TUNNETT (spectrum analyzer)

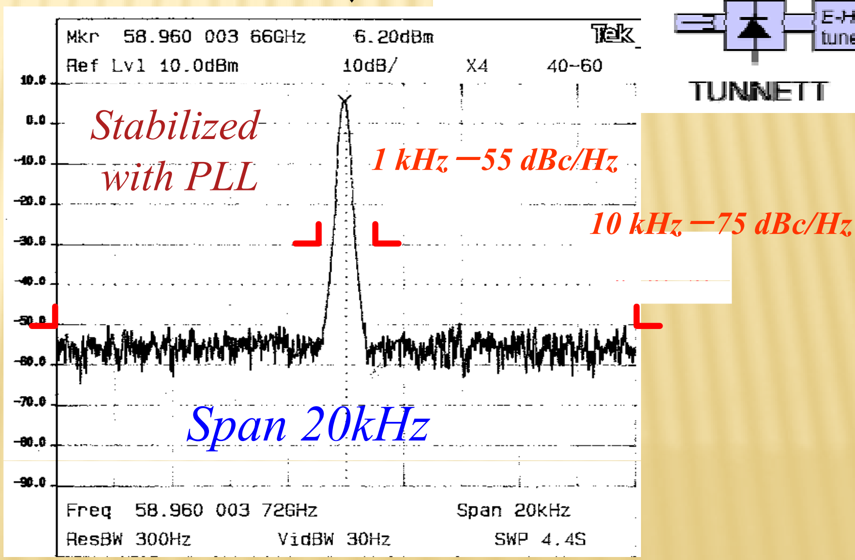


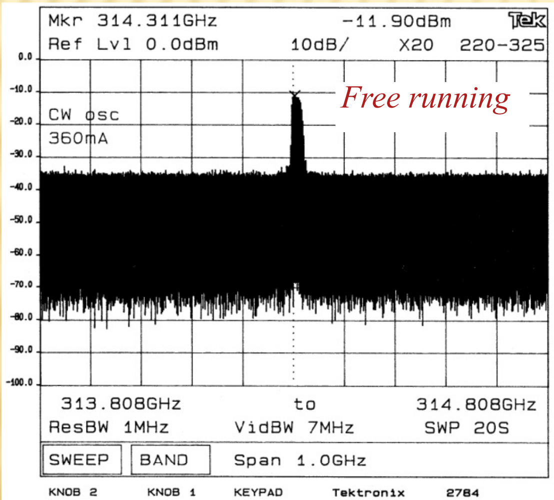
LPE(TDM-CVP)grown TUNNETT
Cavity: WR-15(V-band), 50-75 GHz





PLL
Phase locked loop



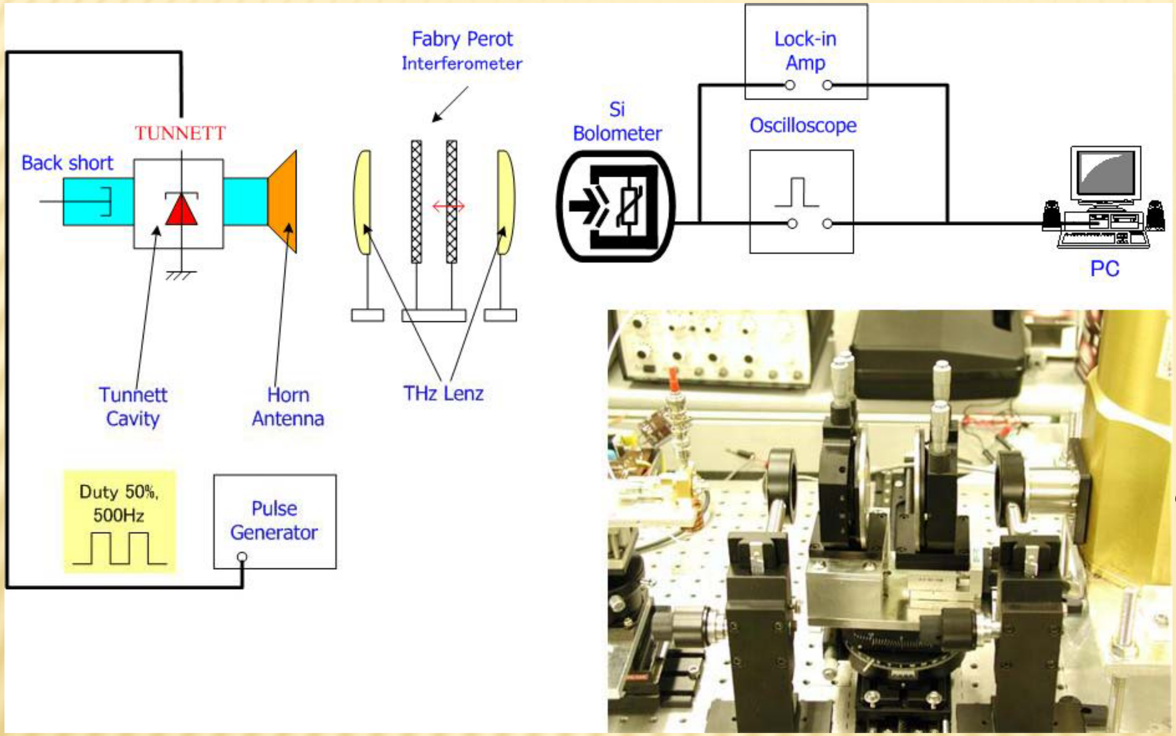


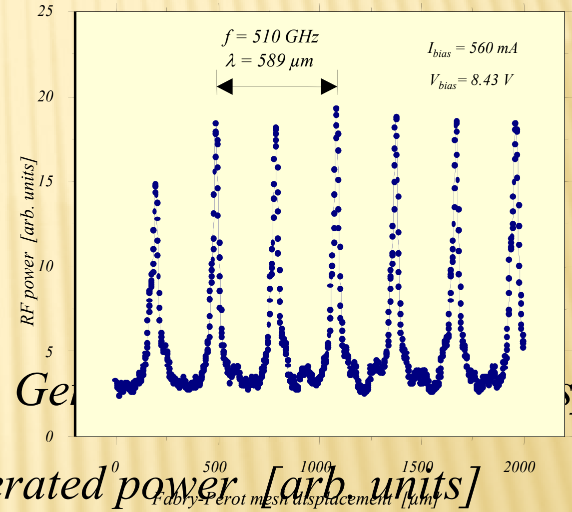
MLE grown TUNNETT
Cavity: WR-03(J-band), 174-325 GHz

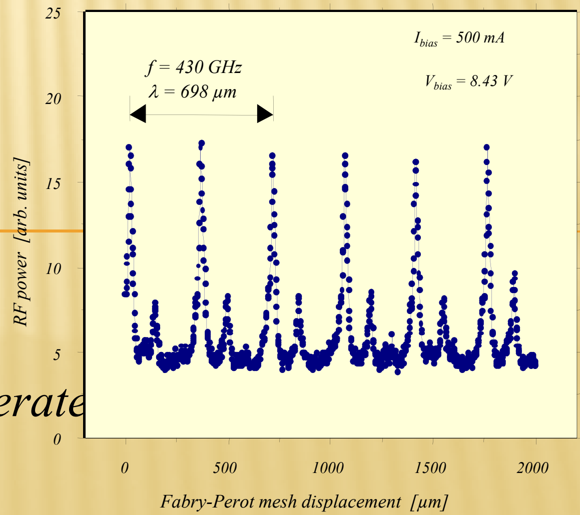
Oscillation characteristics of TUNNETT (Fabry-Perot)

430 - 510 GHz CW, fundamental mode

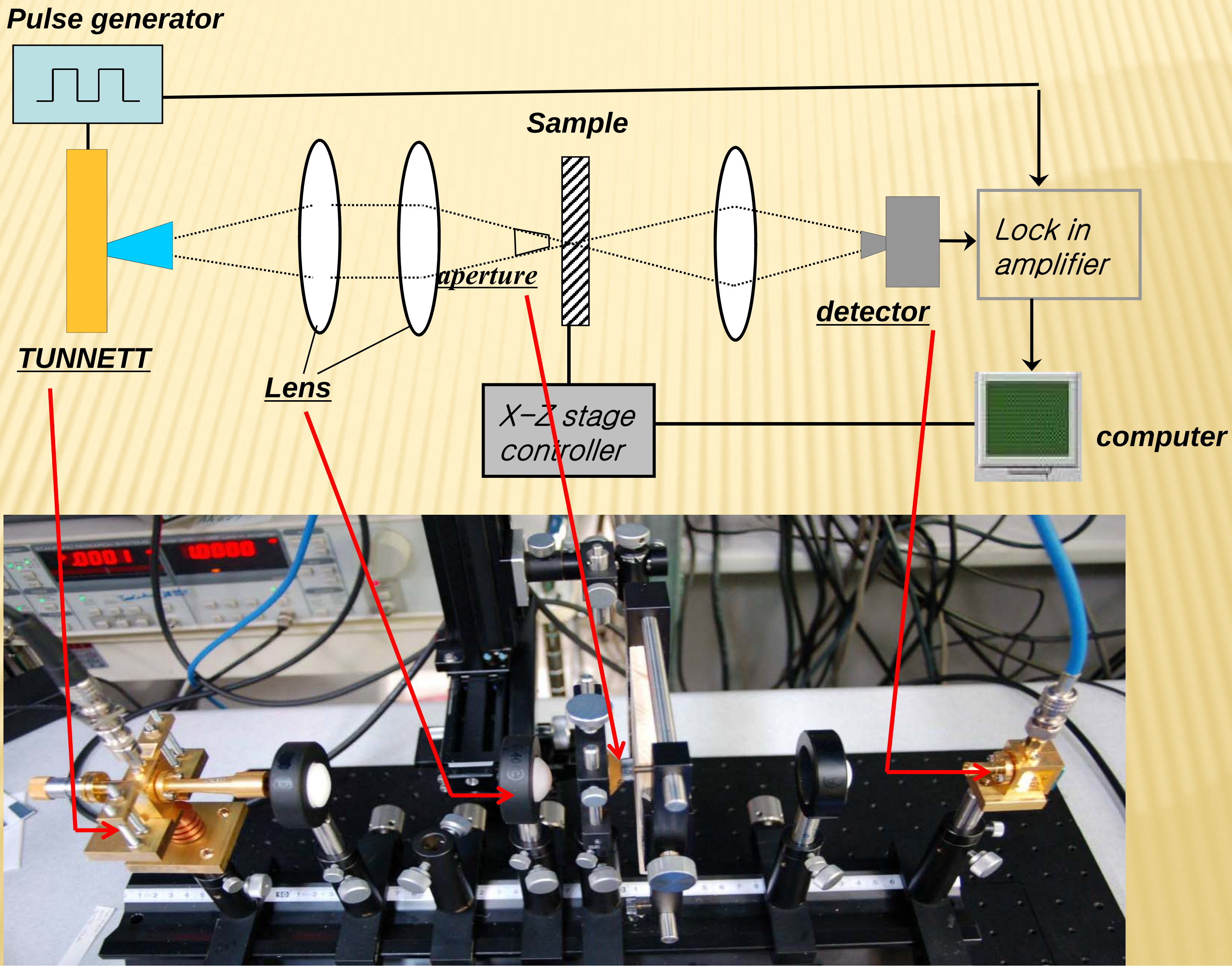
WR-1.5 cavity (0.381 × 0.191 mm)



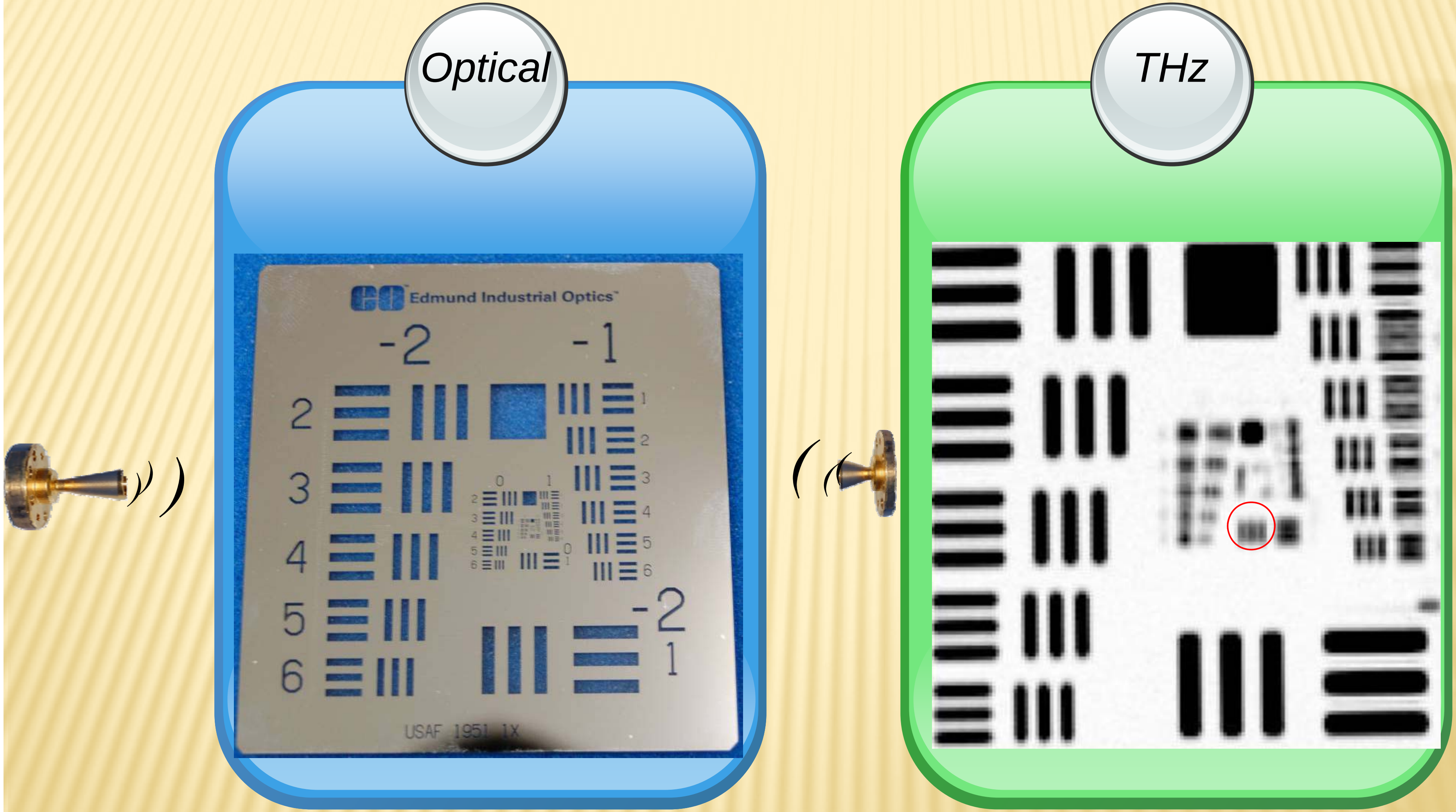




TUNNETT IMAGING SYSTEM

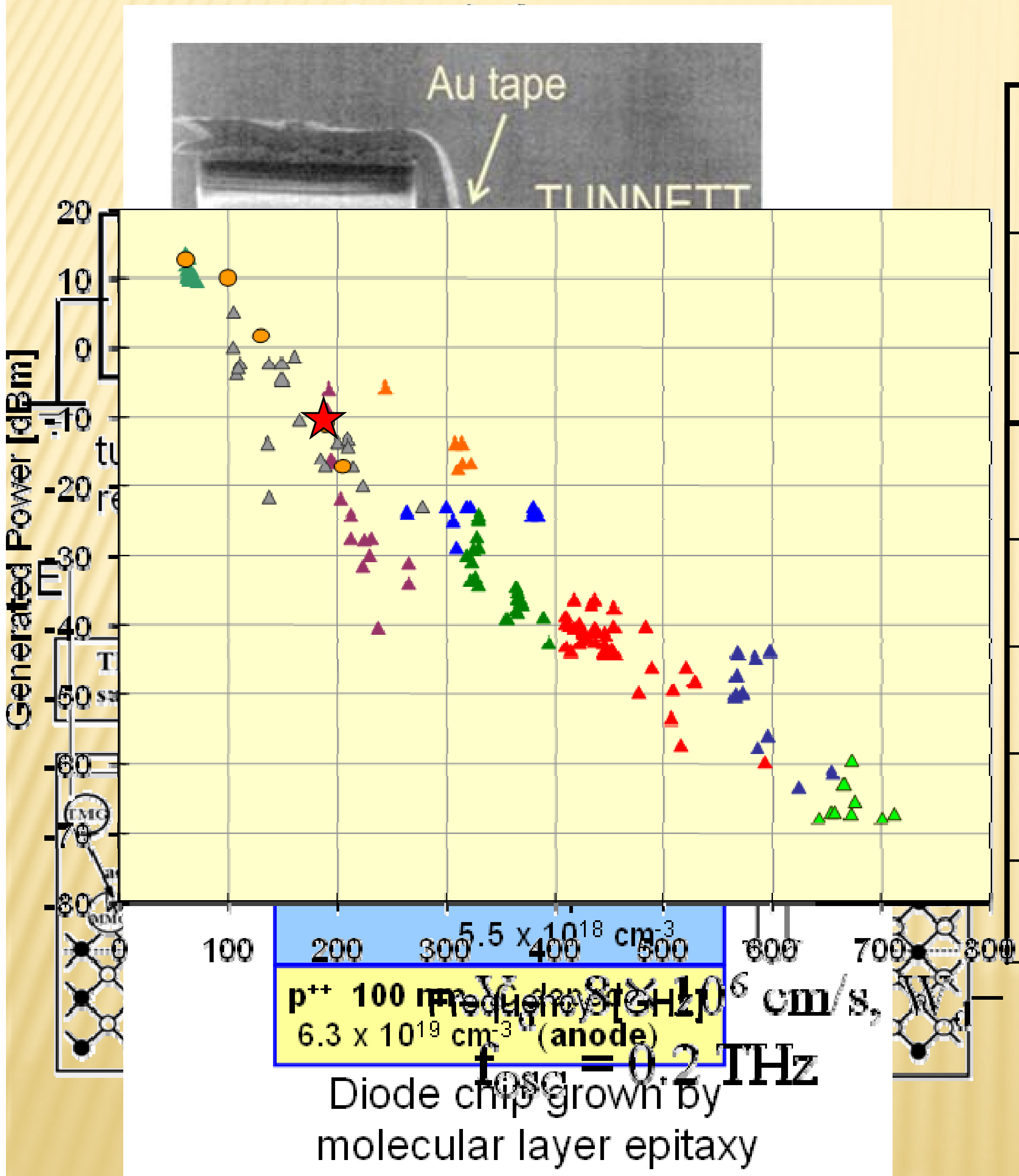


Resolution Demonstration



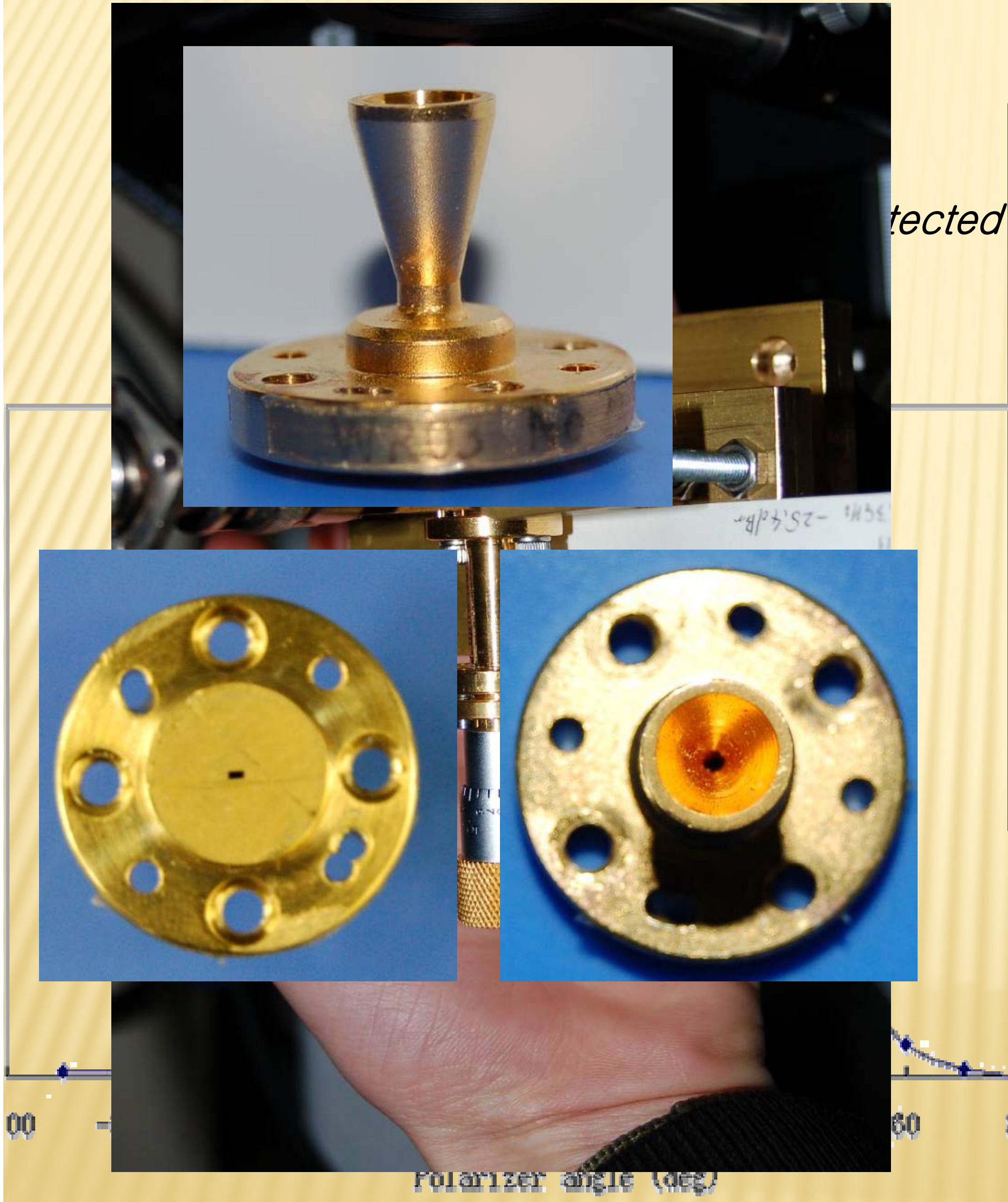
*With a **Φ**1.5mm aperture the highest resolution ~ 1mm (wavelength ~ 1.5mm)*

TUNEETT Performance



TUNNETT	*__tunnel__ injection* *__t__ransit __t__ime diode*
Technics	*Molecular Layer Epitaxy*
Construction	
THz wave form	*CW (RT)* *Pulse (RT)*
Frequency	*~200GHz* *(667m^{-1})*
Line width	*10MHz*
output	*~-10dbm* *(0.1mW)*
power stability	*<0.1%/hr*

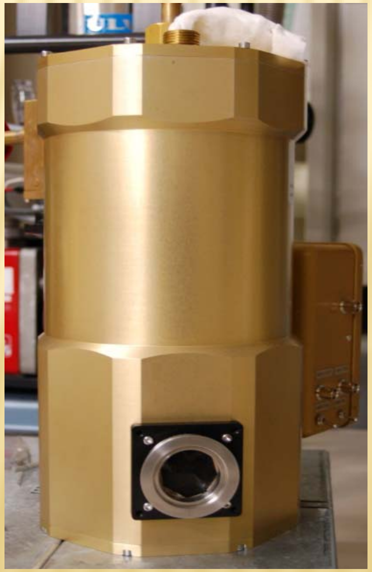
TUNEETT Oscillator

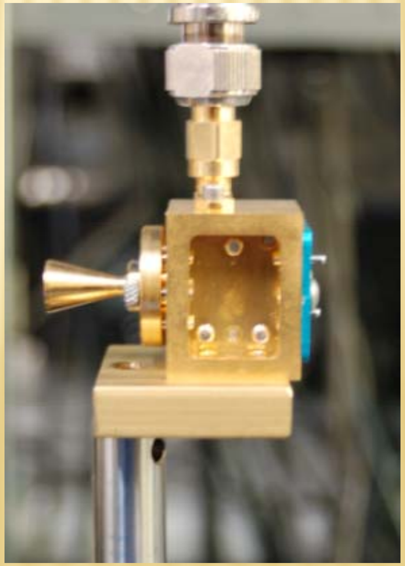


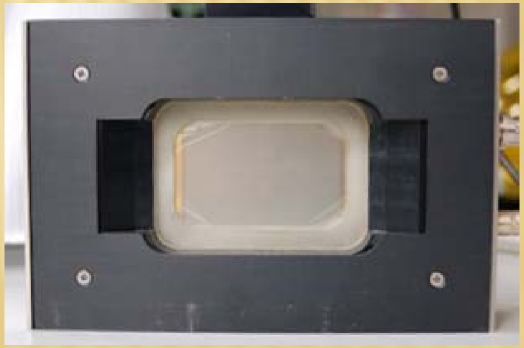
Size	*115 ×30 ×60mm*
Waveguide Resonators	***WR-2.2:0.559 ×0.279 mm (rectangular)***
Polarization	***Linear (rectangular waveguide)***

THz Detector in Imaging System

Detector	*Si-Bolometer*	*SBD detector*	*Thermometer*
Sensitive	*High* *(>10 times higher than SBD)*	*Medium* *(10 times higher than thermometer)*	*Low*
Advantage	*High sensitive* *none-polarized*	*Compact* *Polarization changeable*	*Large receiving area*
Disadvantage	*Need cooling* *(4K Helium)*		*Low sensitive*



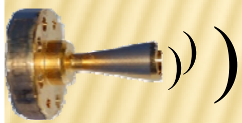


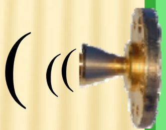


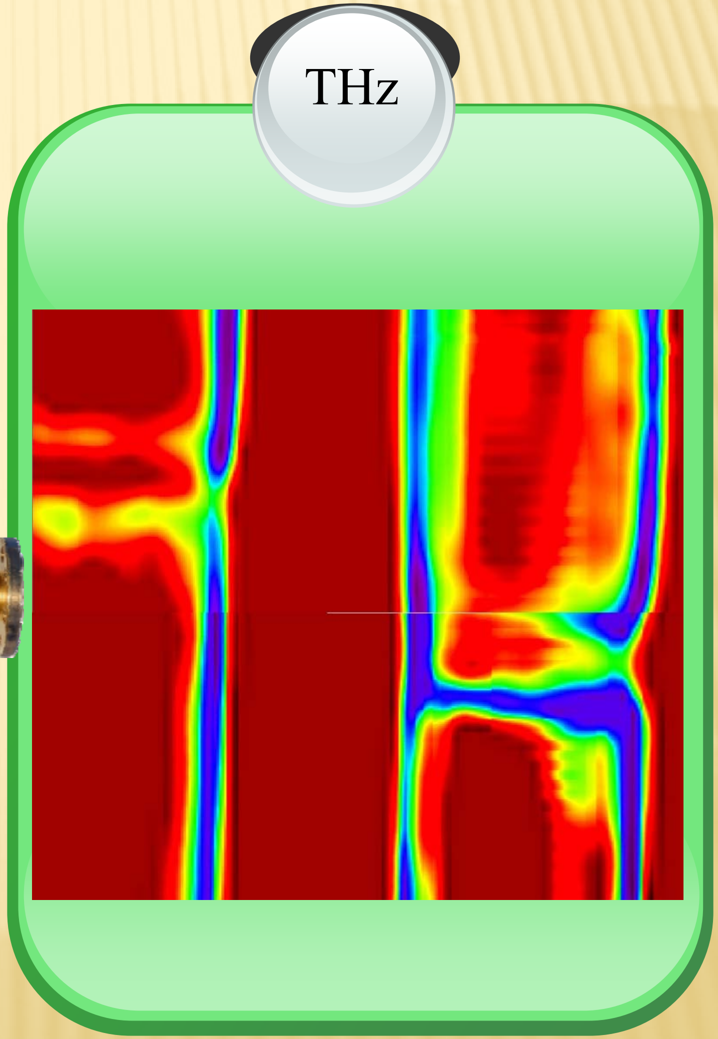
Non destructive Inspection of Defects in Woods

Bamboo Joints

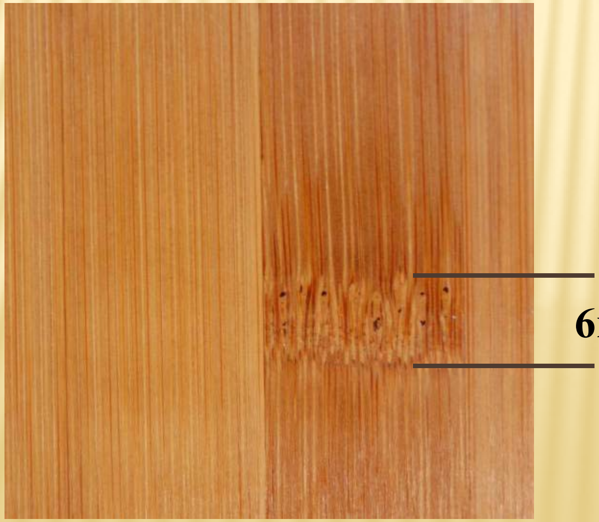
Front







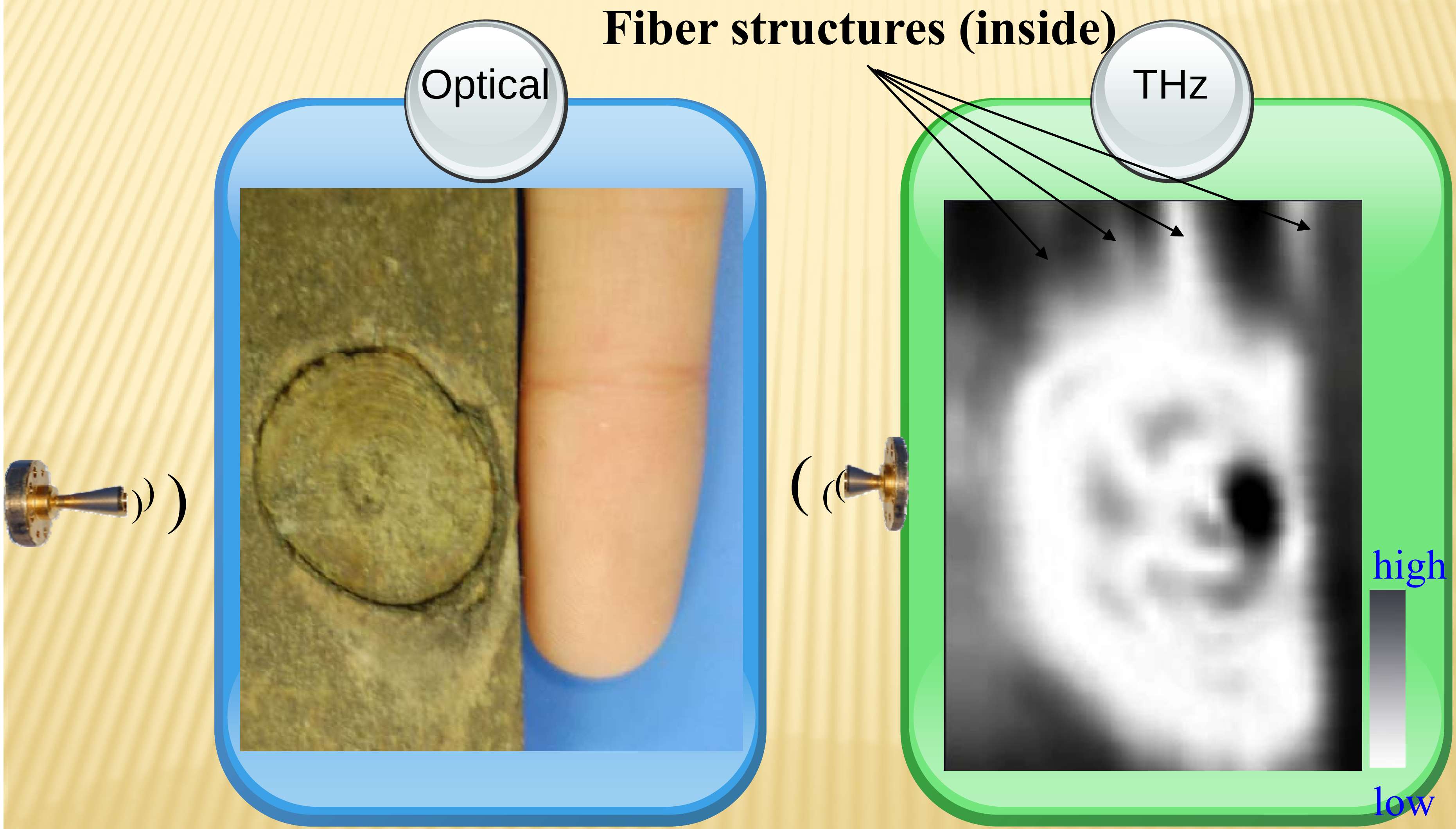
Back



6mm

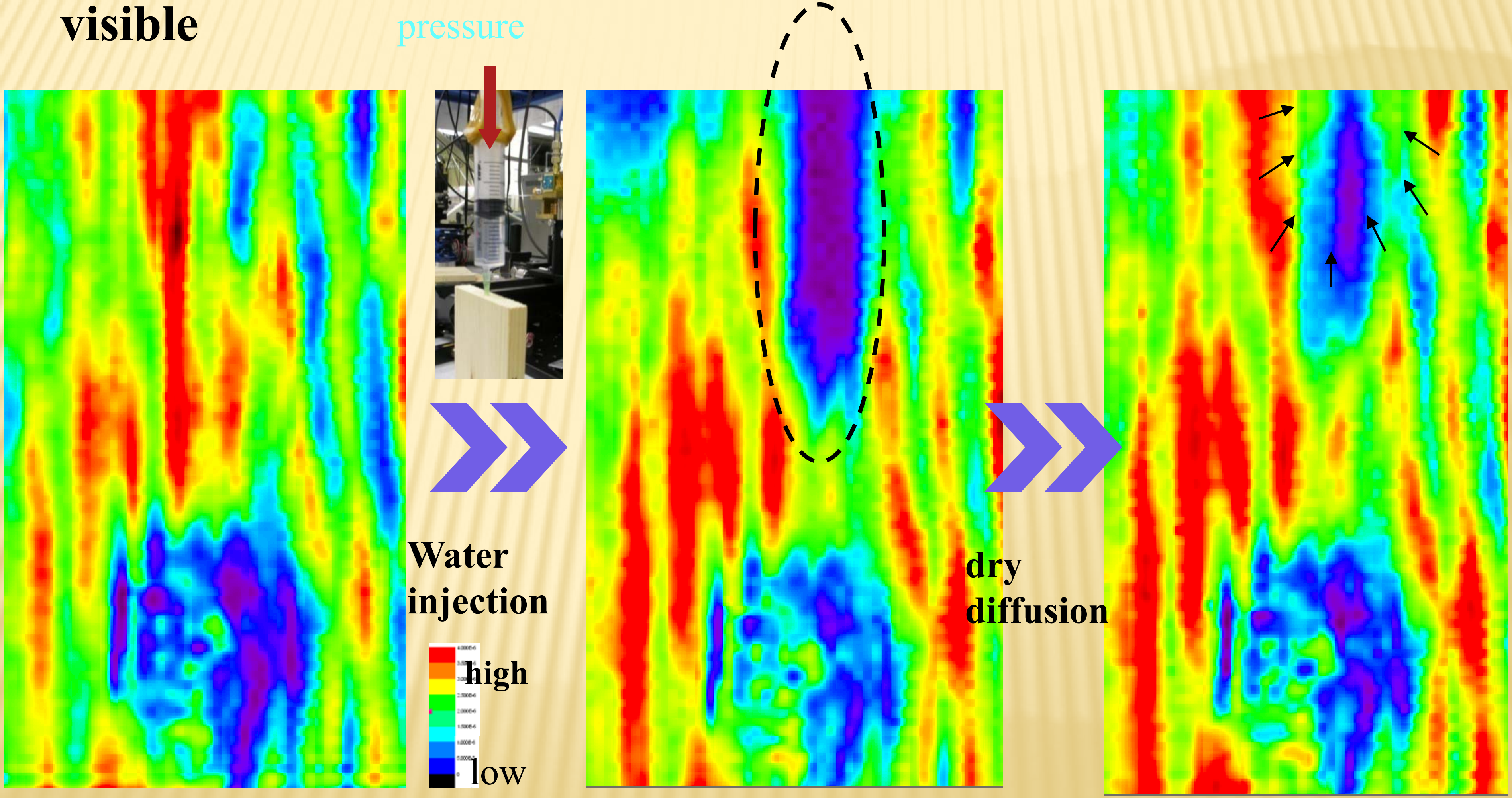
Images Demonstration: defect structure inside wood (not only surface)

A wood knot of sugi

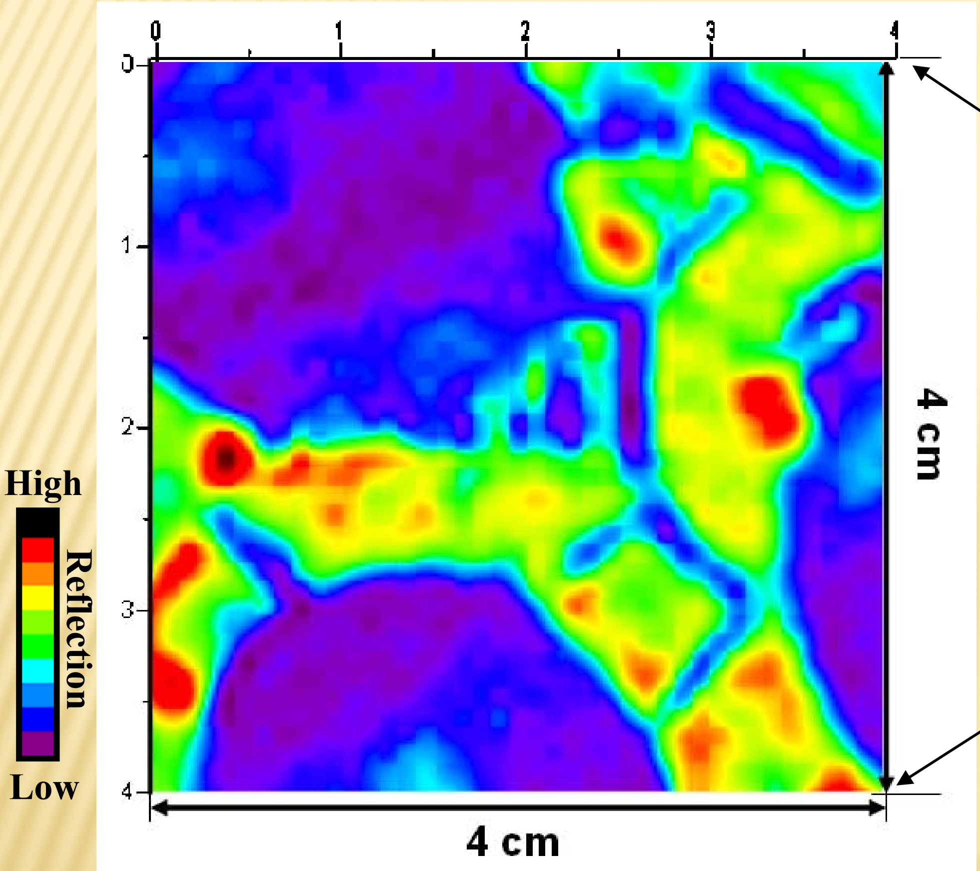


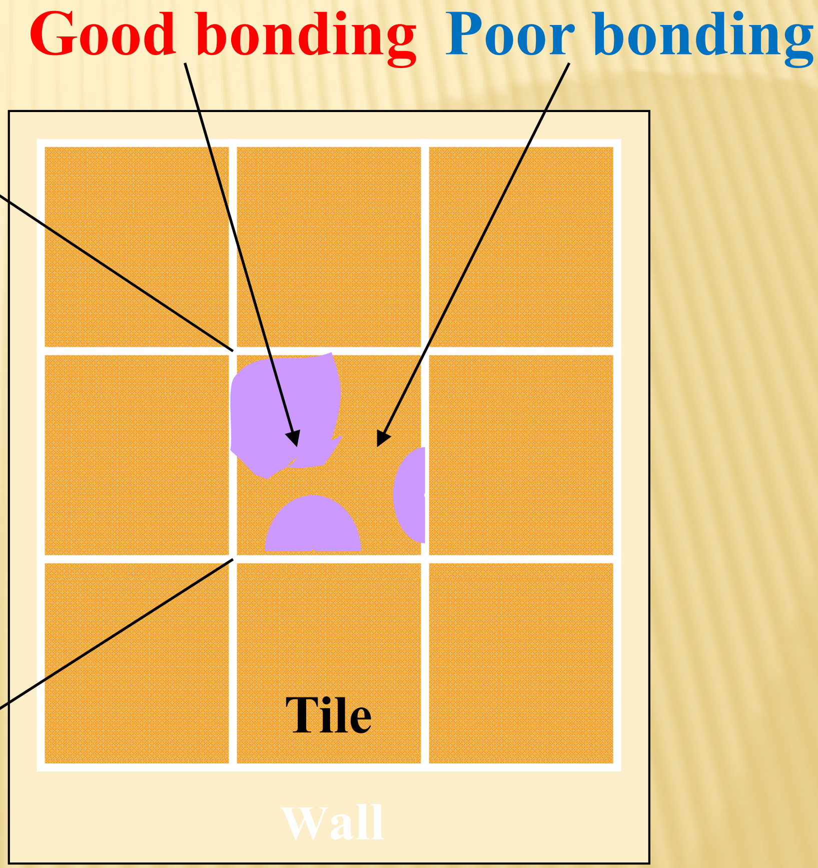
Images Demonstration

So not only special structure (fiber structure, knot)can be seen, but also WATER DISTRIBUTION in WOOD is visible

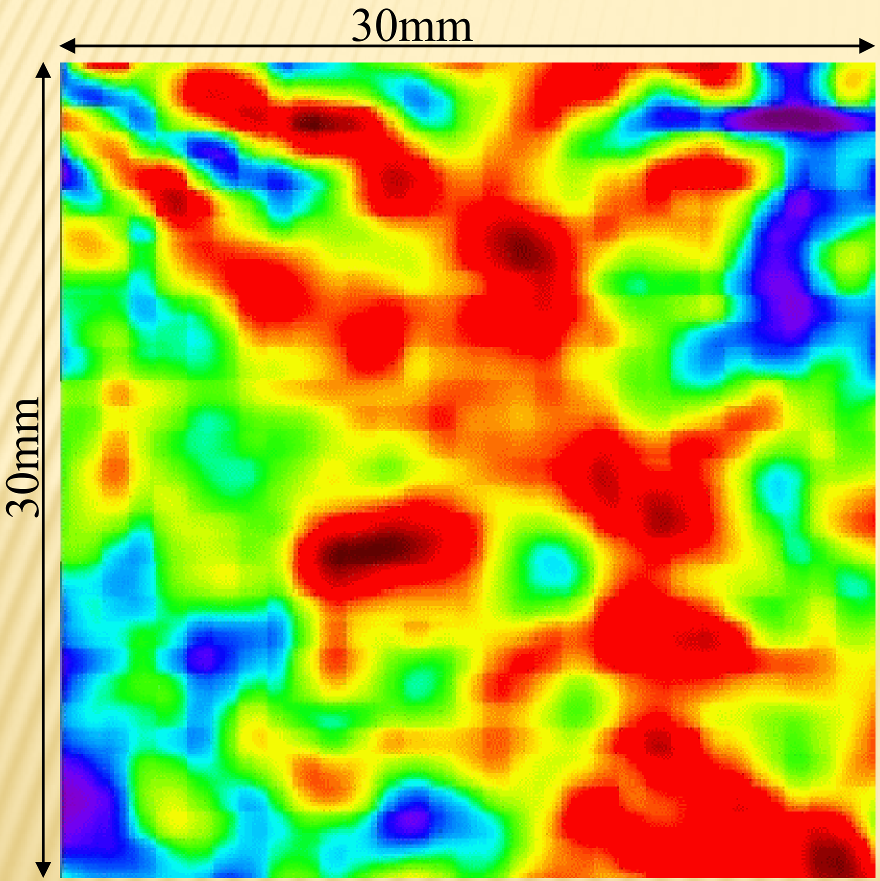


Adhesive defect imaging between ceramic tile and wall





Water diffusion into concrete

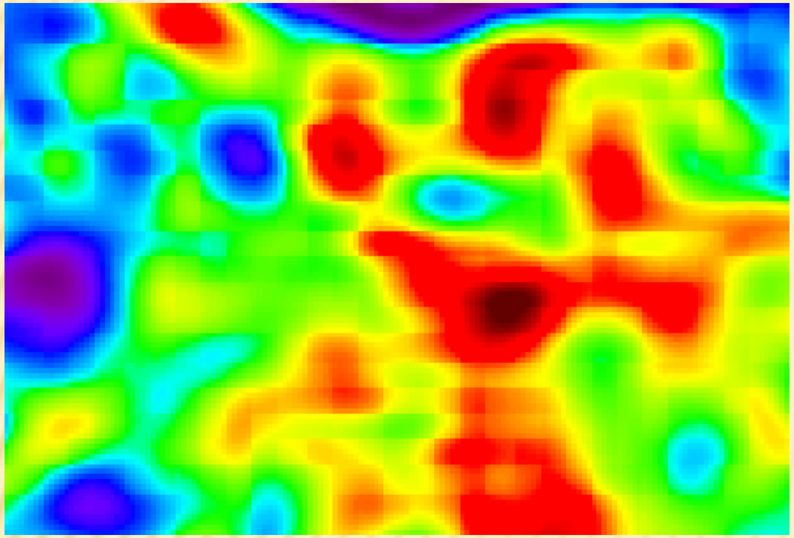


Colorful animation of water diffusion in 1 hour
Concrete thickness= 10mm

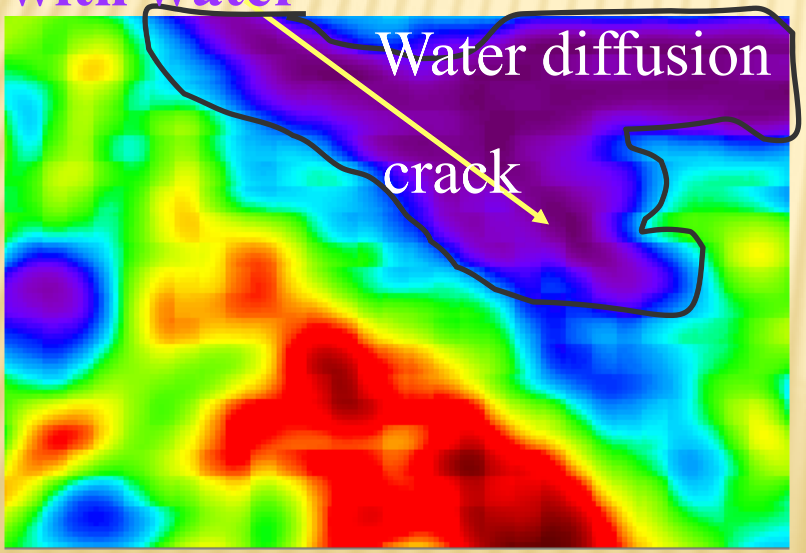
Sample picture

Water diffusion in concrete crack

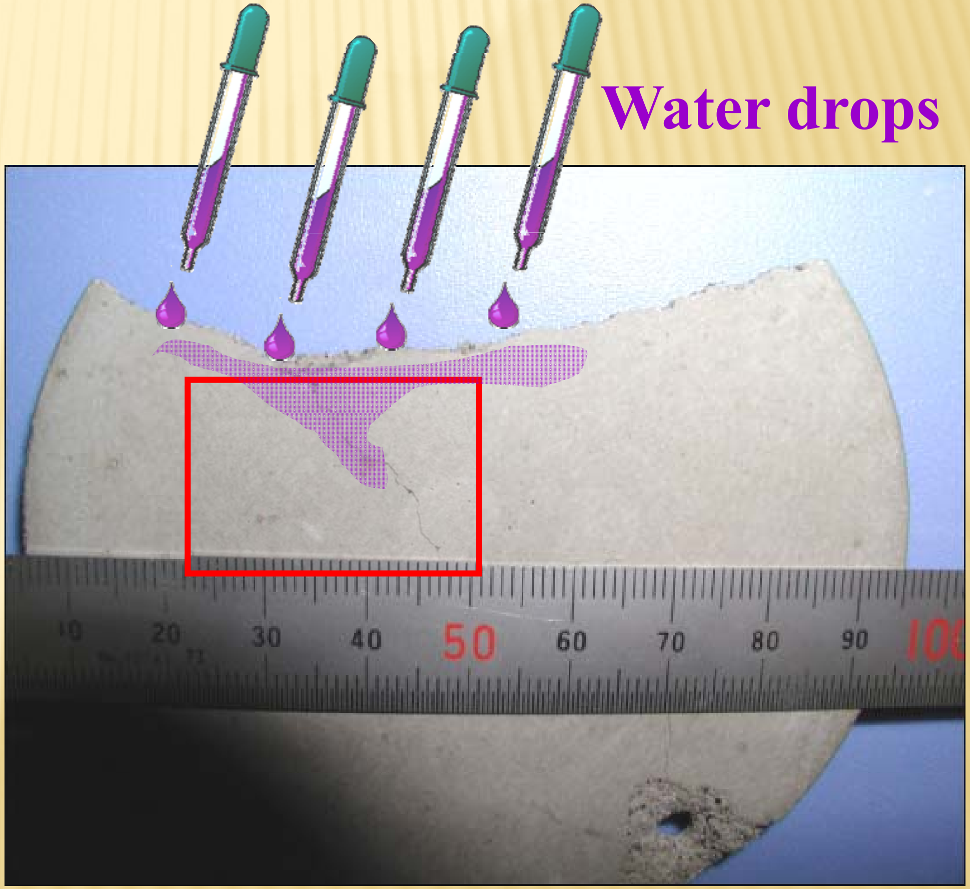
no water



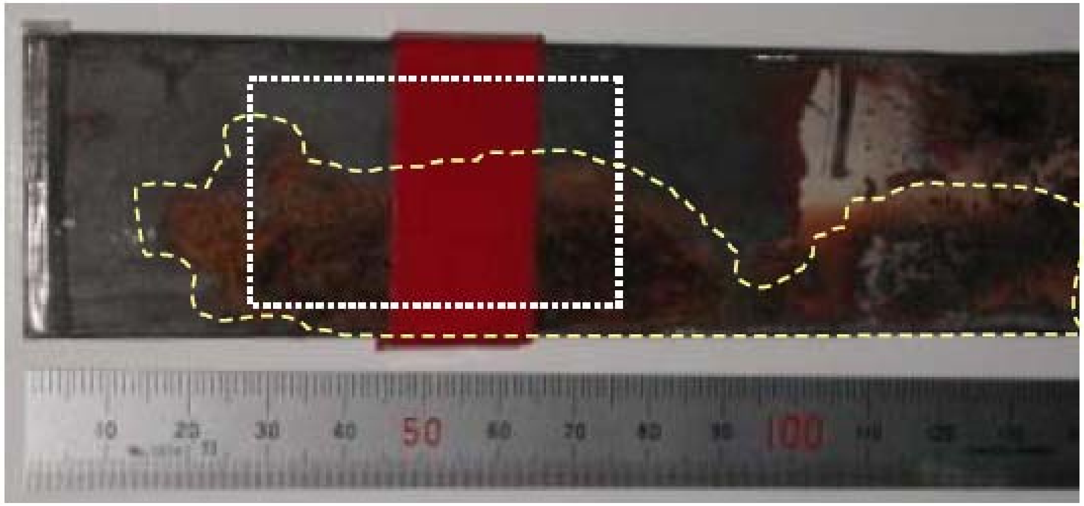
with water



Water diffuses faster in crack than ordinary,
This can be used in crack inspection
Water can be served as "enhancer" for crack inspection



Stain distribution imaging under coating of coated steel (reflection imaging)



visible

Plastic coating thickness 0.2mm

Plastic coating thickness 1.0mm

THz imaging

Outline

Analysis of GaSe growth mechanism

GaSe solution growth
by temperature difference method
Under controlled vapor pressure

Evaluation of optical aspects
PL, NIR & THz spectroscopy

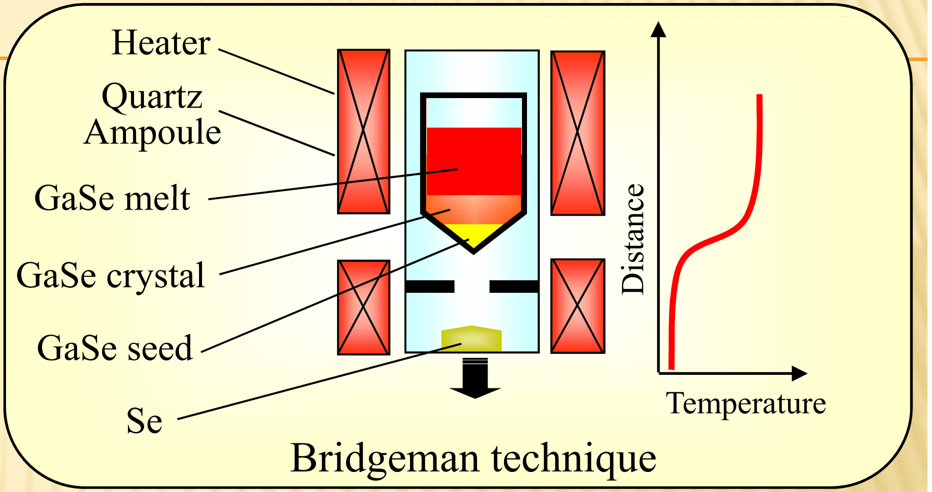
Evaluation of defects
and dislocations
XRD

Application for THz wave generation
DFG via collinear phase matching

Crystal Growth of GaSe (conventional)

GaSe crystal using THz-wave generation

Growth by Bridgeman technique



～Problems of Bridgeman technique～

- **Mechanical disturbance during crystal growth**
- **Introduction of defects and dislocations by thermal stress**
- **High Se vapor pressure (15atm) at melting point (938℃)**
- **High temperature growth: Point defect density is high**

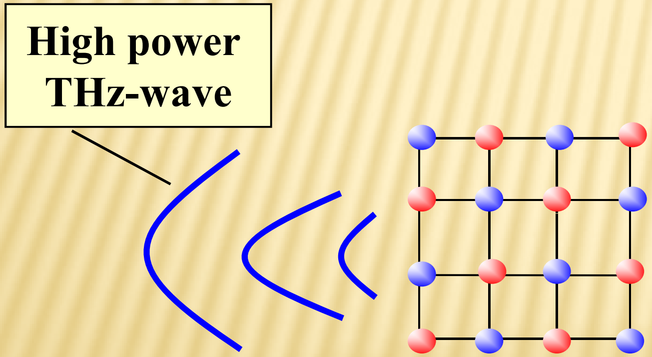
Reduction of THz-wave power

Perfect crystal growth technique is required for THz generation

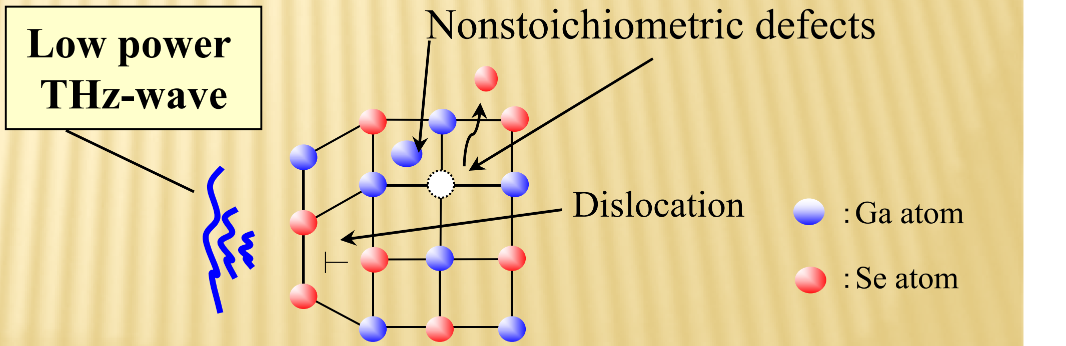
For higher output power of THz-wave

- Stoichiometry controlled crystal growth technique
- Reduction of nonstoichiometric defects in GaSe crystal

Temperature difference method under controlled vapor pressure (TDM-CVP)



GaSe perfect crystal

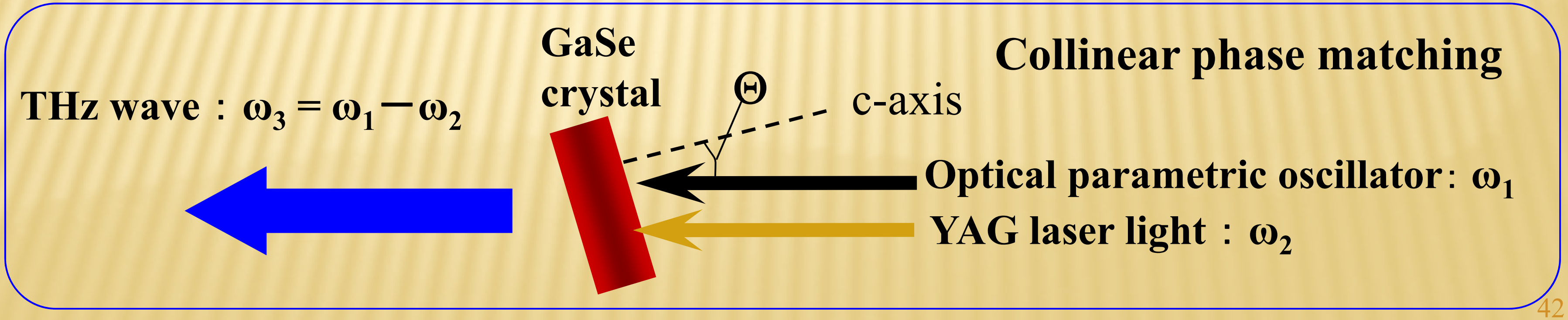


GaSe crystal contained nonstoichiometric defects and dislocations

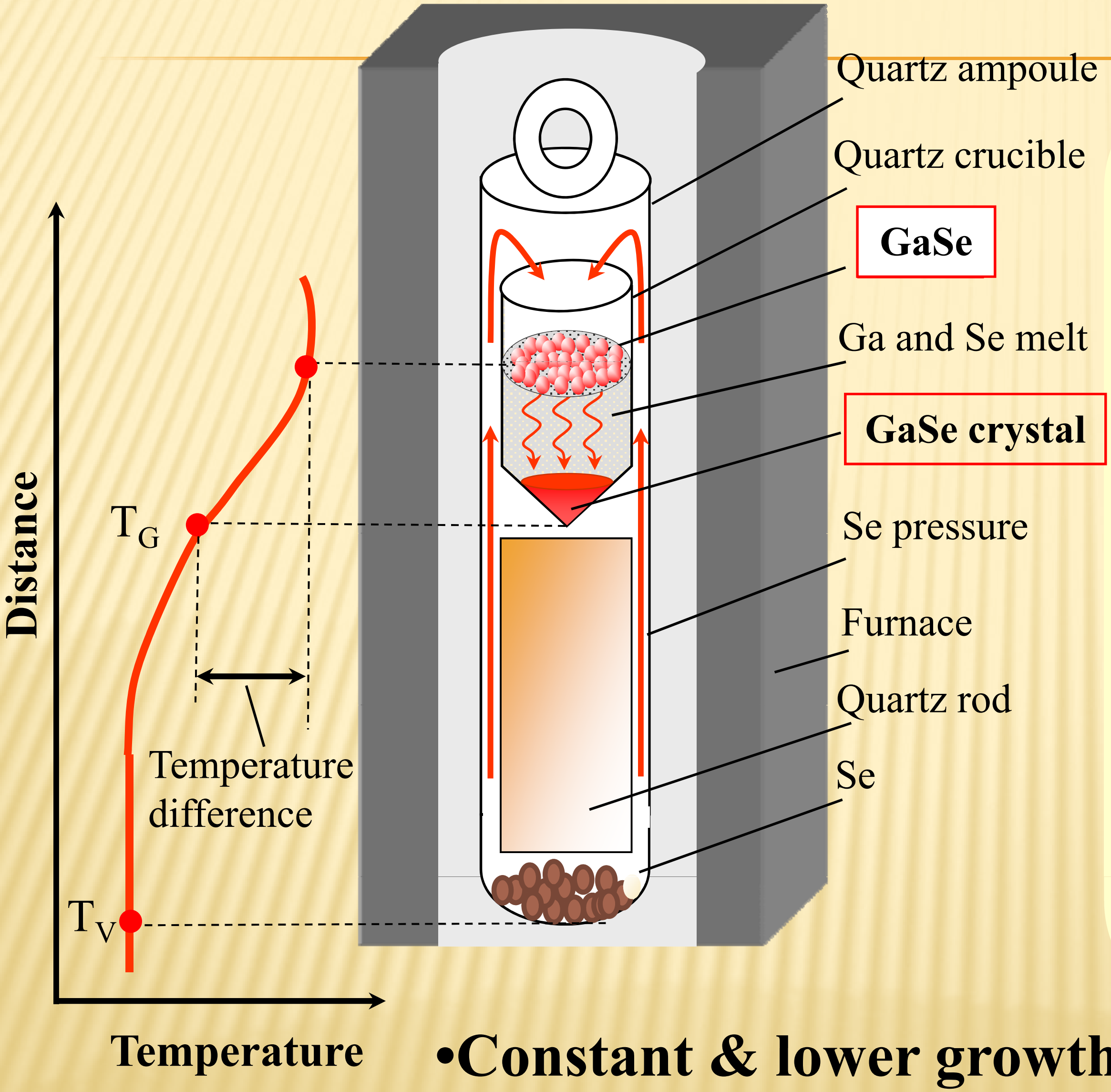
Mission

Improved quality of GaSe crystal

- **GaSe crystal growth by TDM-CVP**
- **Improved transmission characteristics in near-infrared (NIR) and THz-frequency region**



Temperature difference method under controlled vapor pressure



Width of Se vapor path
< Mean free path of Se molecule

$$P_{Se} = P_v \sqrt{\frac{T_G}{T_v}}$$

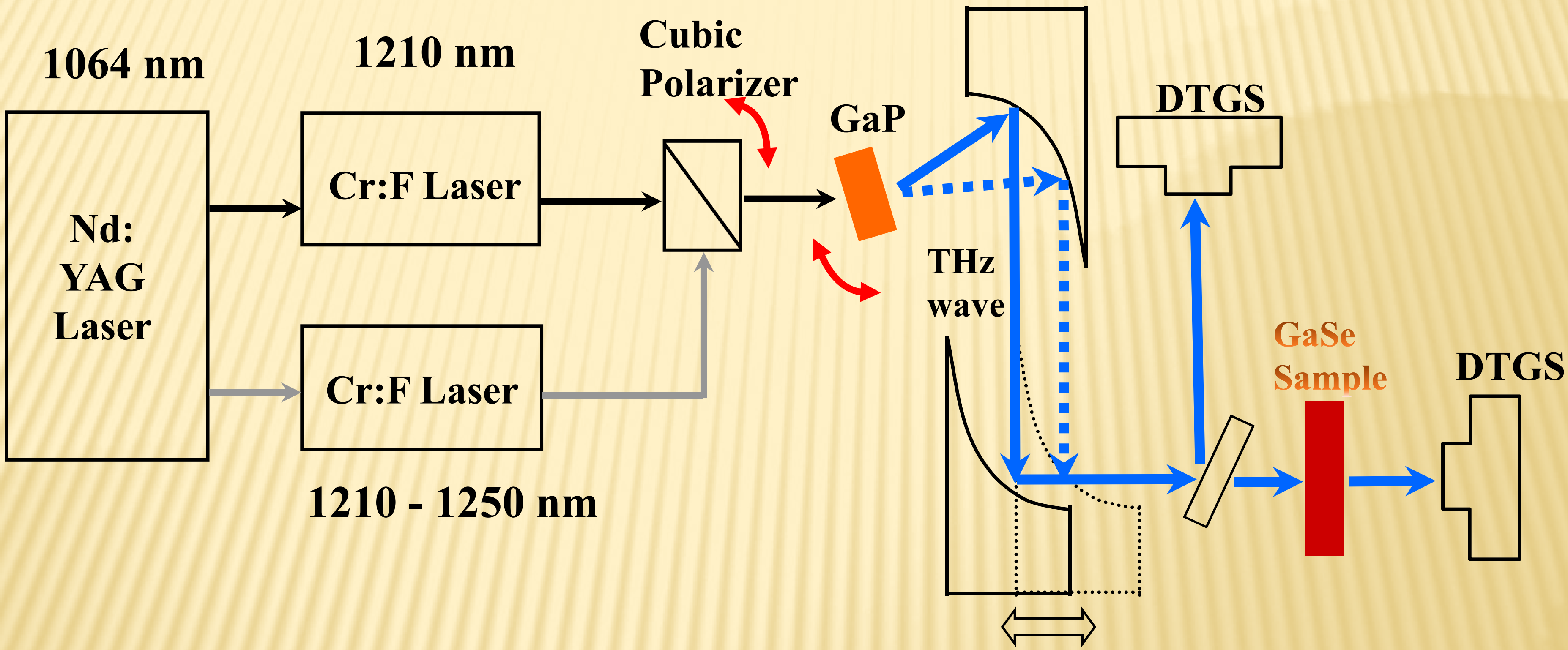
P_{Se}: Applied Se pressure
T_G : Growth temperature
T_V : Low temperature portion
P_V : Se pressure at T_V

- **Constant & lower growth temperature**
- **Se vapor pressure control (stoichiometry control)**

Experimental procedure

- **Growth conditions**
  - **Growth temperature : 530~590℃**
  - **Temperature gradient : 15 ~ 26 ℃/cm**
  - **Applied Se vapor pressure : 7.74×10^{-7}, 0.00104, 7.75 Torr**
  - **Growth time : 7 ~ 32 days**
- **Evaluation**
  - **Surface morphology by optical microscope**
  - **X-ray diffraction analysis**
  - **Photoluminescence (PL) excitation : Ar^{+} laser**
  - **Absorption spectra in NIR and THz-frequency region**
  - **THz generation via DFG (collinear phase matching)**

GaP THz spectrometer (double beam configuration)
For THz absorption spectroscopy



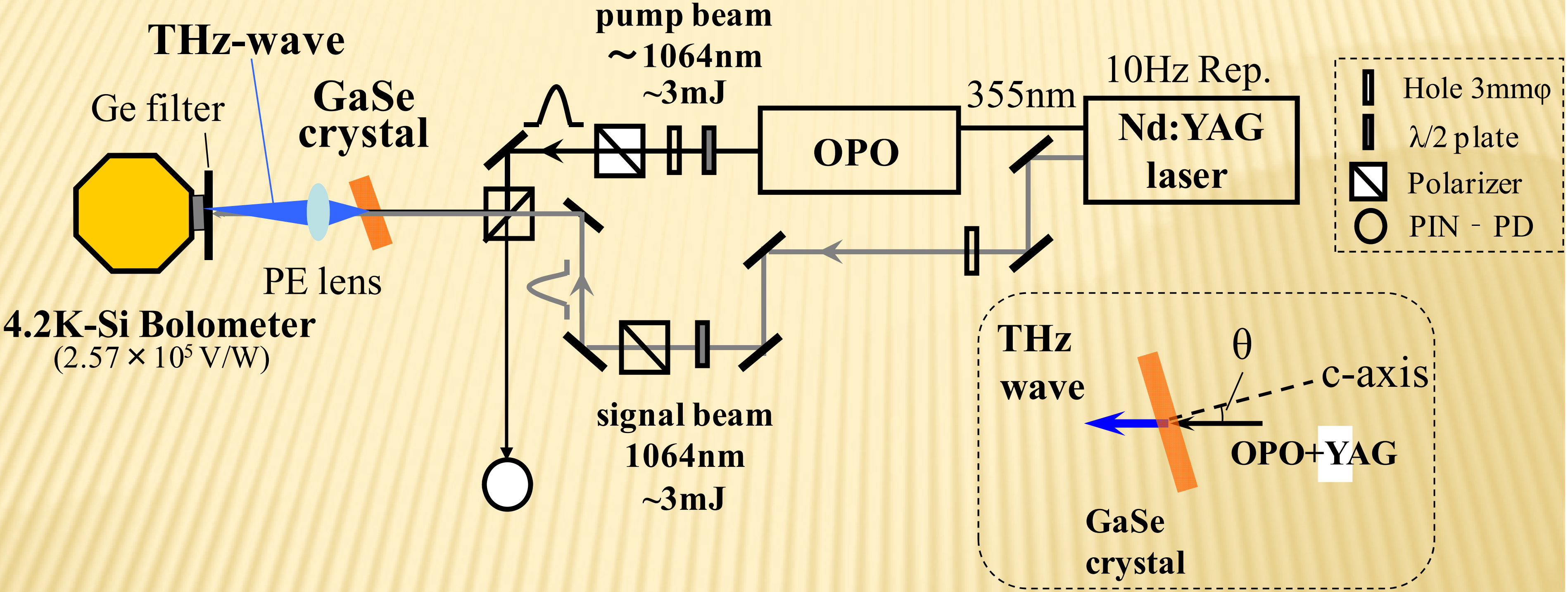
Incident light ：Cr:forsterite lasers (wavelength：1210nm, 1210~1250nm)

Detector ：DTGS detector (RT operation)

Coherent THz wave: 0.1~7THz (maximum power ~1.5W)

with Δf~100MHz

Experimental setup for THz generation



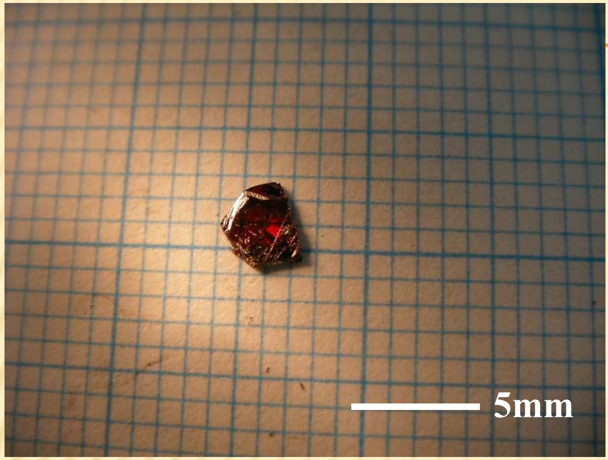
- sample: undoped-GaSe(001): thickness of 2 mm
- beams: pump: OPO (optical parametric oscillator)

  λ:1042nm－1064nm、power ～3mJ、linewidth 6GHz、pulse duration 6ns

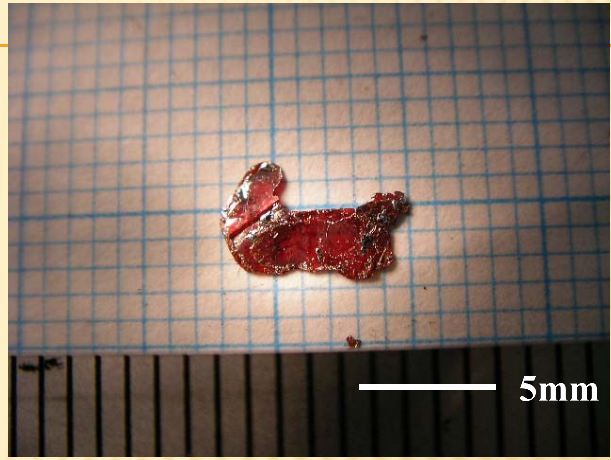
  signal: Nd:YAG laser

  λ: 1064.2nm、power ～3mJ、linewidth 90MHz、pulse duration 11ns
- detector: liquid-helium-cooled Si bolometer

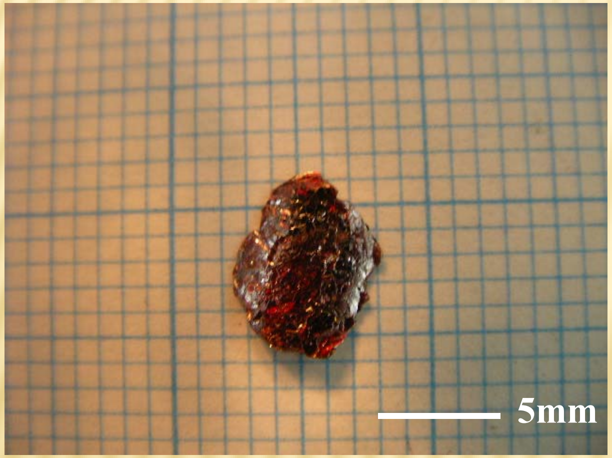
Grown crystals



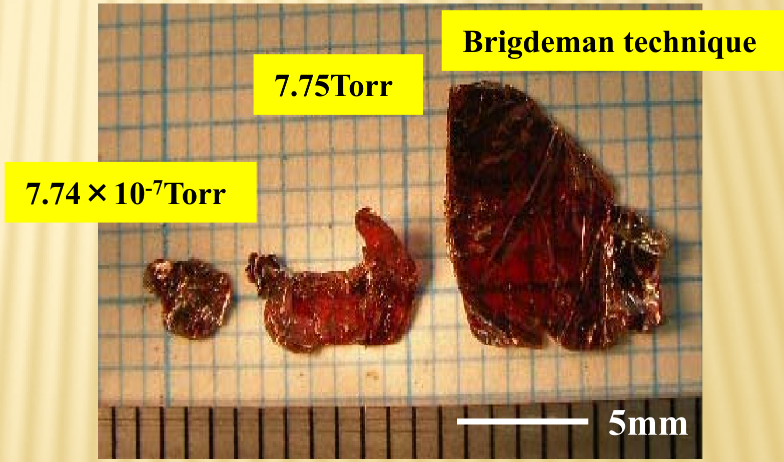
(a) P_{se} = 7.75Torr (Thickness : 313μm)



(b) P_{se} = 7.75Torr (Thickness : 160μm)



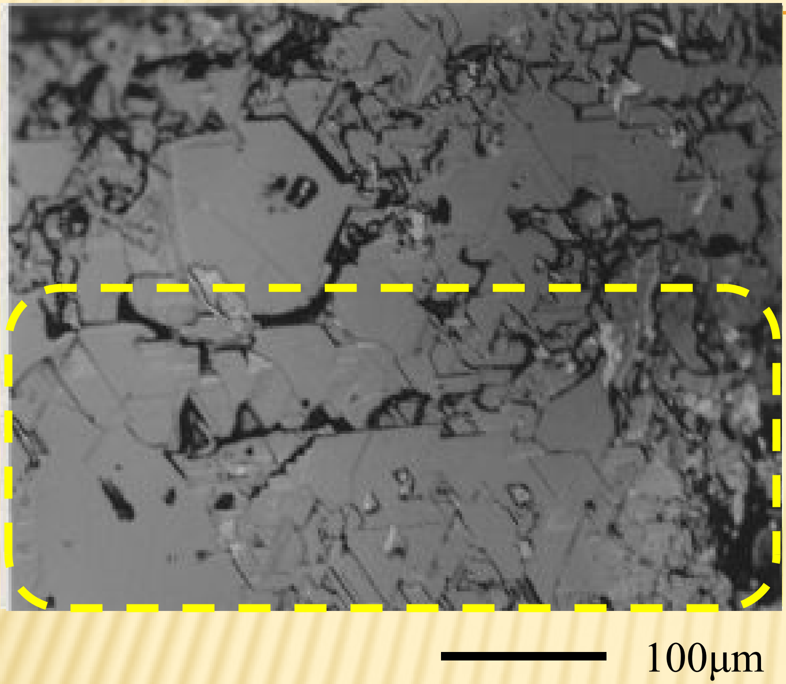
(c) P_{se} = 0.0104Torr (Thickness : 356μm)



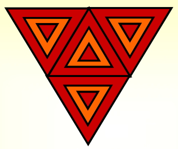
(d) Comparison between TDM-CVP and Bridgeman technique

➡ **Growth of transparent GaSe crystals by TDM-CVP**

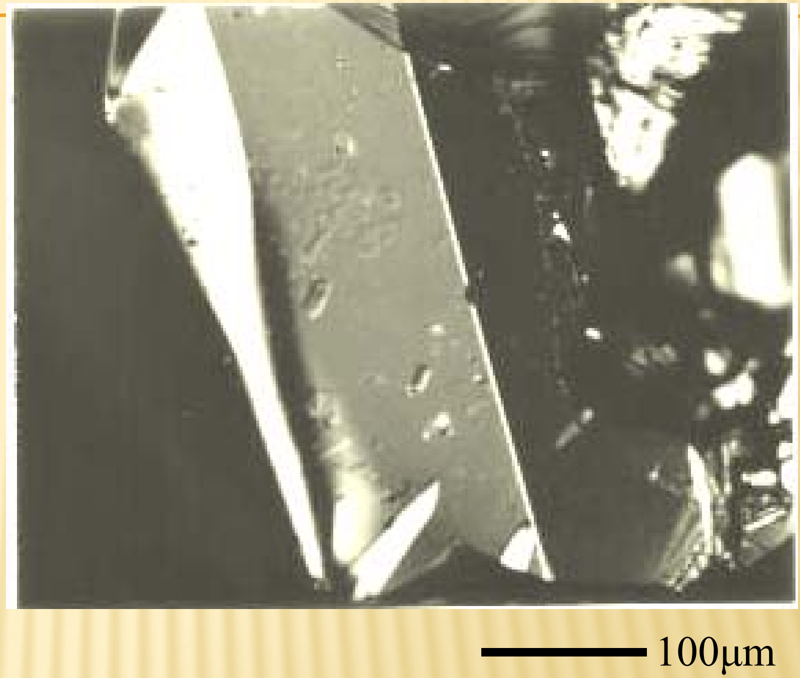
Surface morphology



(a) Triangular islands on GaSe surface



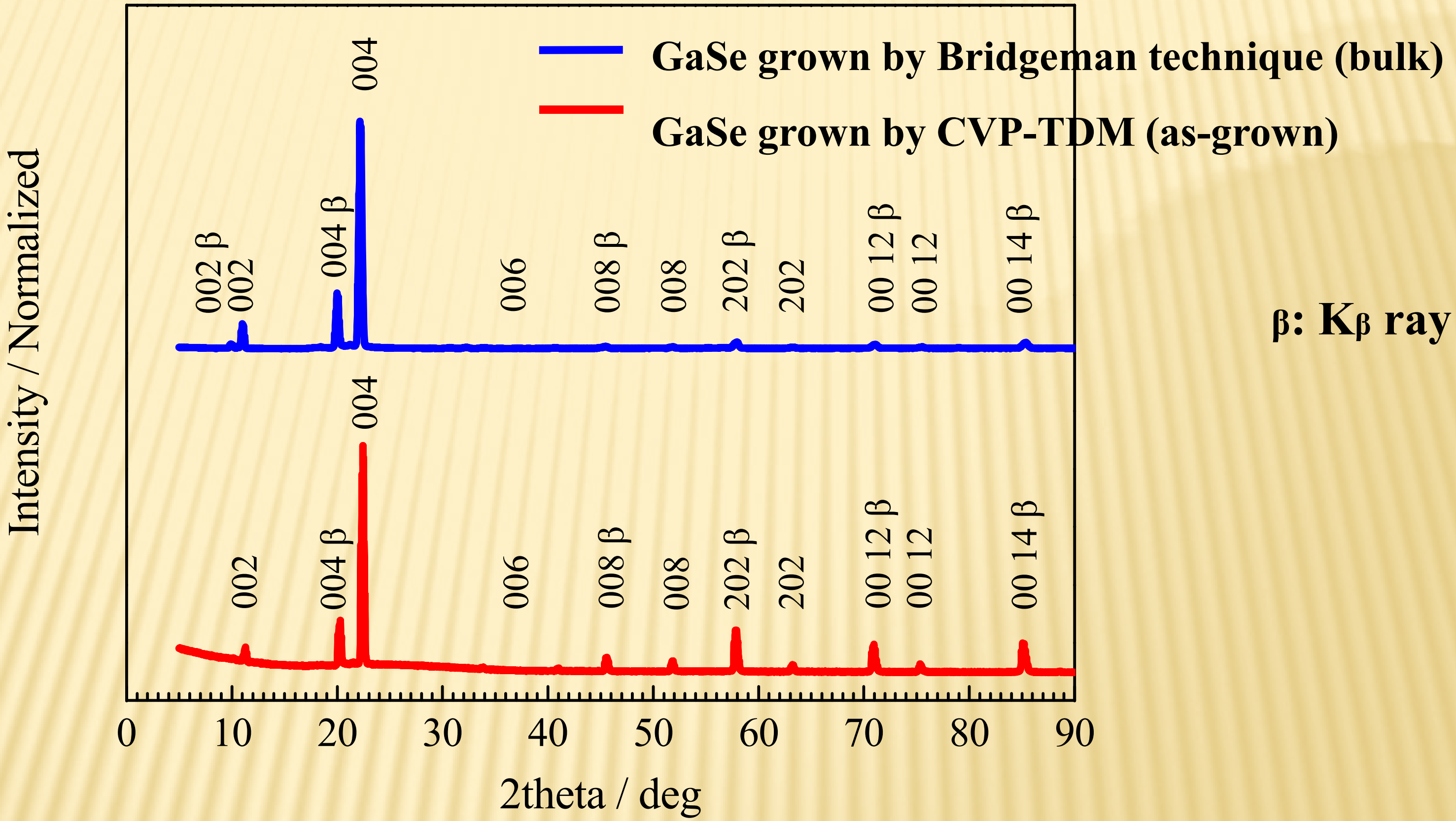
Observed triangular islands on GaSe surface



(b) Surface of GaSe grown under Se vapor pressure (7.75Torr)

Flat surface of GaSe grown under Se vapor

X-ray diffraction pattern

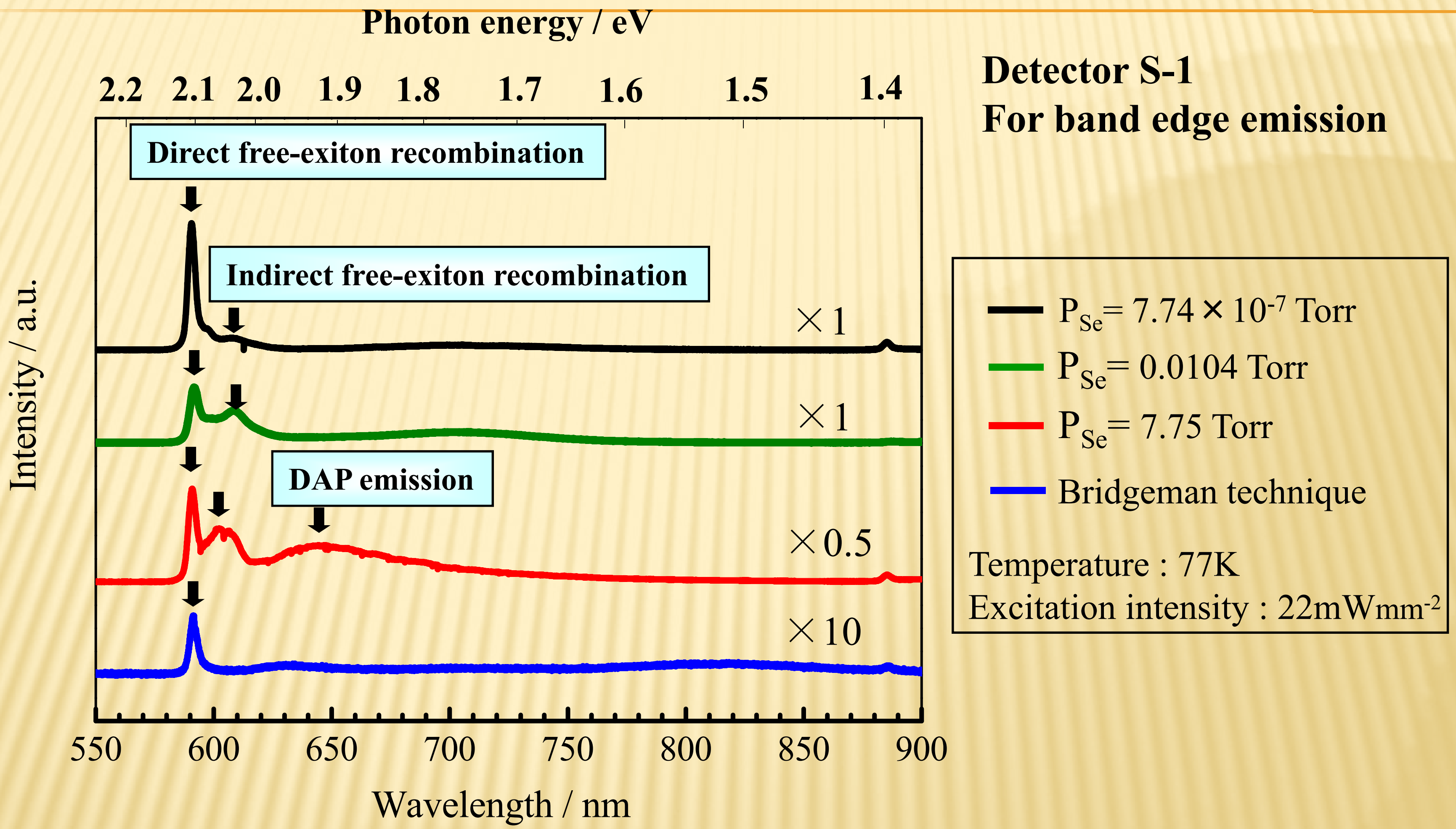


β: Kβ ray

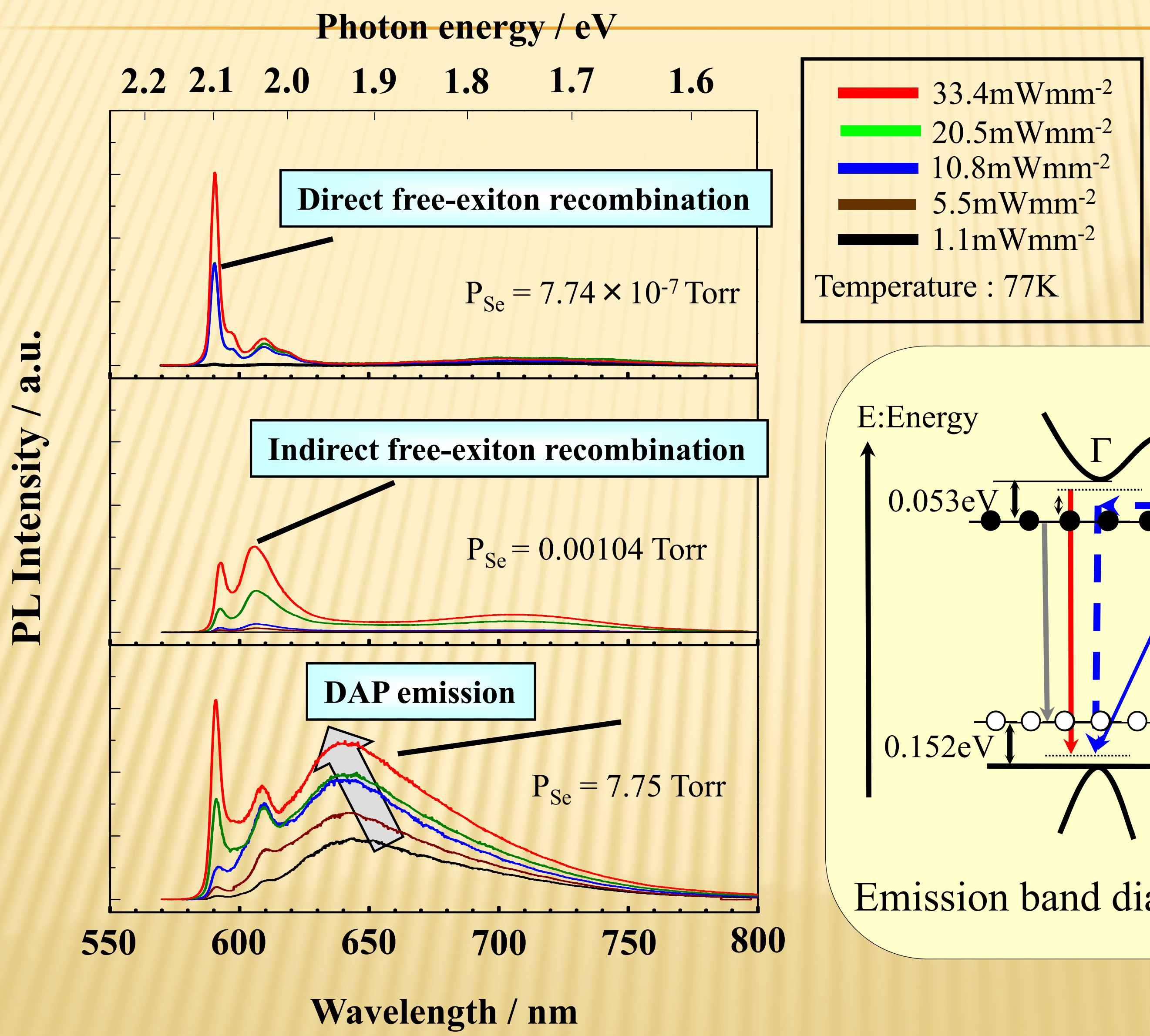
Crysatal phase and polytype → **Hexagonal ε type**

Dominant diffraction peak of c plane → **Growth of GaSe single crystal phase with (001) plane**

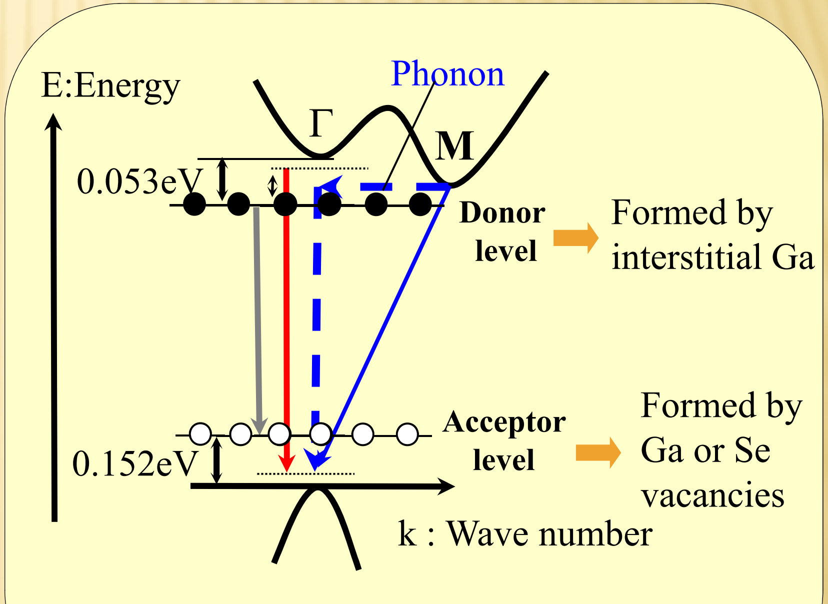
77K-PL spectra of GaSe samples grown under different Se pressures



Excitation intensity dependence of 77K-PL spectra

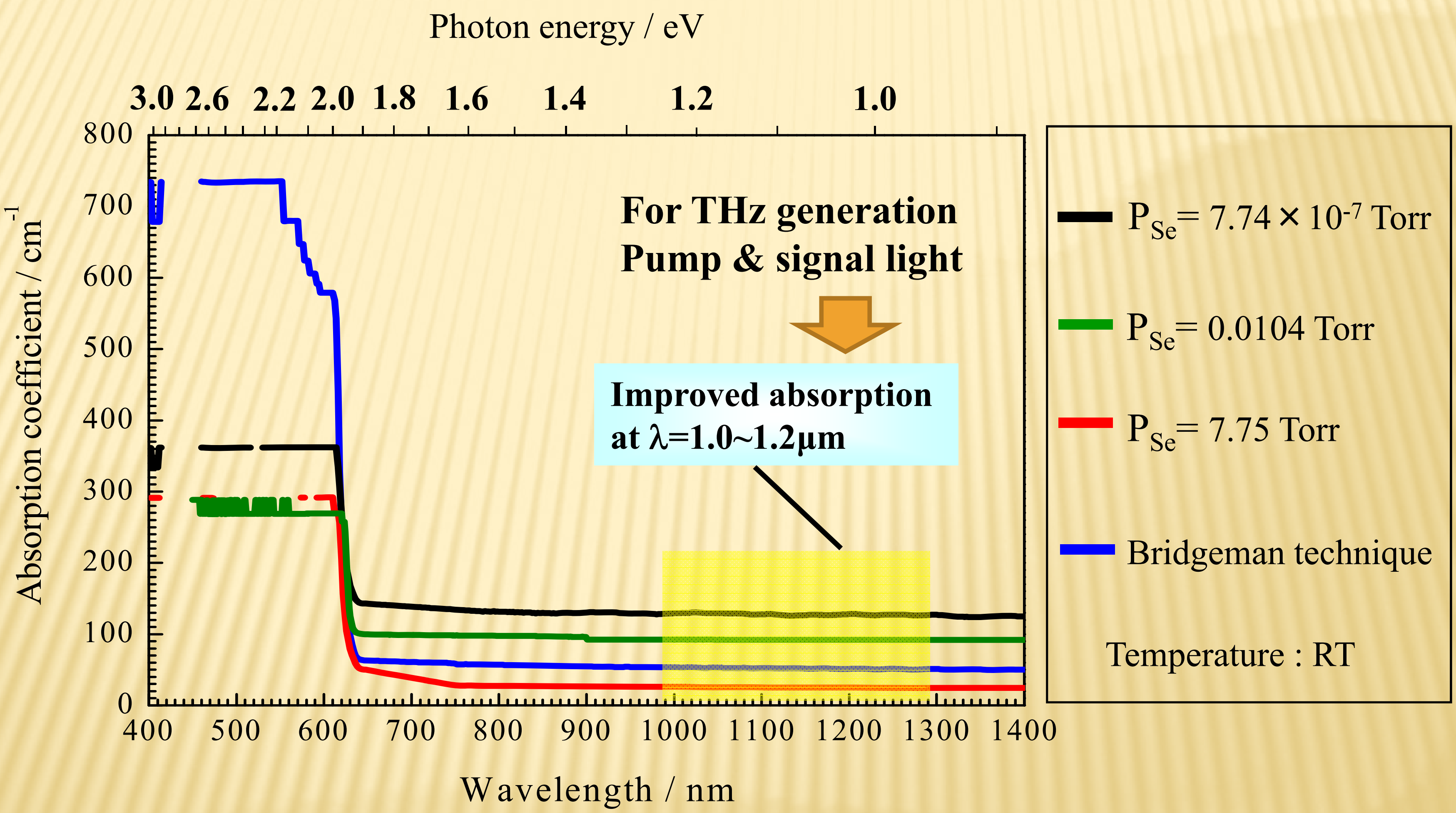


Detector: cooled Ge
For deep level emission

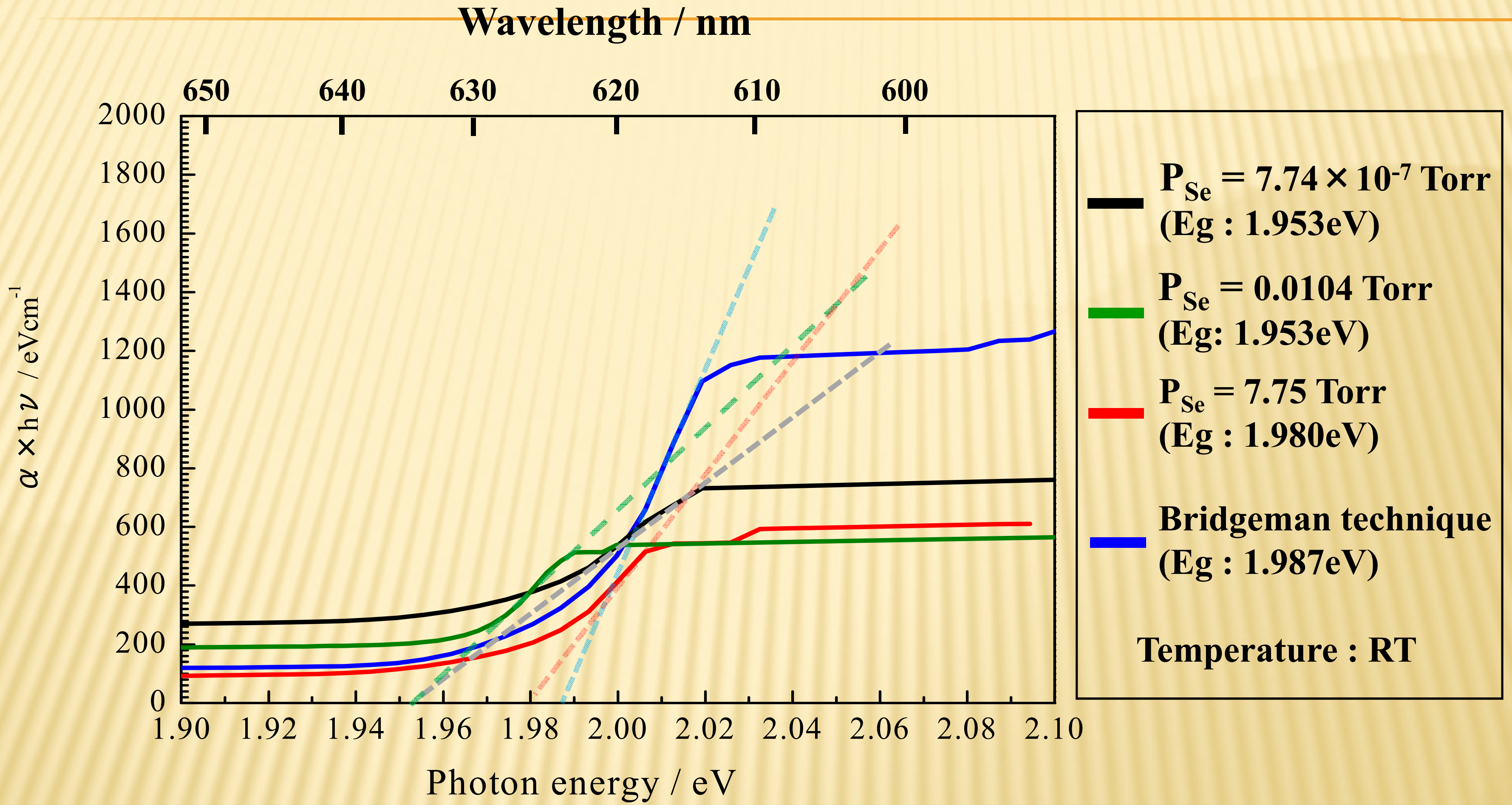


Emission band diagram in GaSe

NIR Absorption spectra



Optical Band gap energy of TDM-CVP grown crystals



Band gap of TDM-CVP growth samples

➡ **ε-GaSe band gap at RT (2.004eV)**

THz Absorption spectra

Improved absorption by free carrier reduction

Improved absorption by phonon

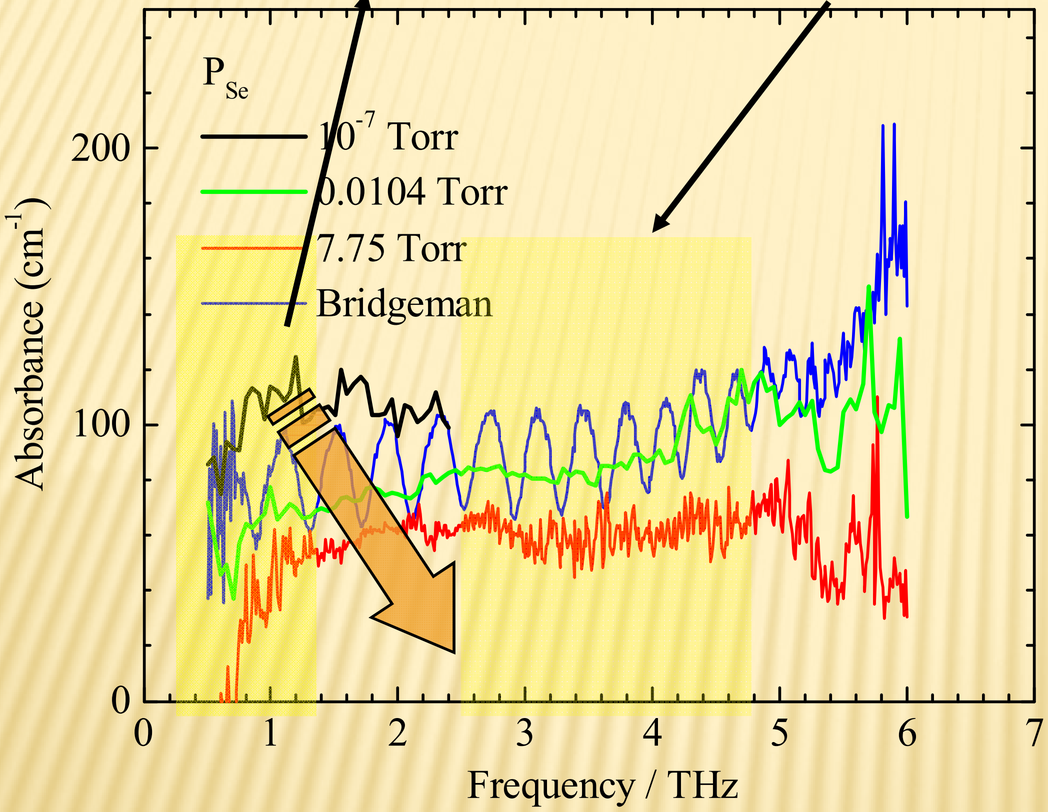


Figure 6 THz absorption spectra of the grown crystals. That of Bridgeman grown sample is also shown as a reference

Improved absorption
By the reduction of inter-molecular vibration (Defective)

Resonant Frequency

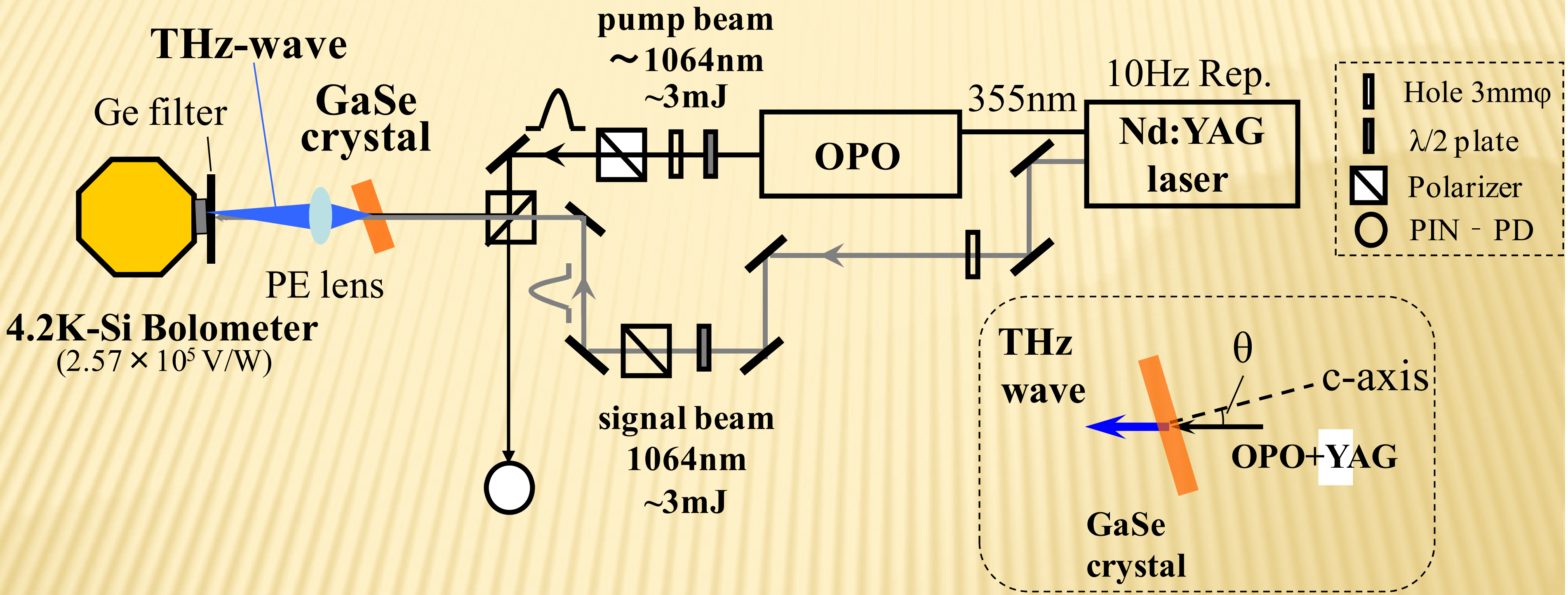
As P_{Se} increases

Shift to higher frequency

→ Tightly bonded layered strct.

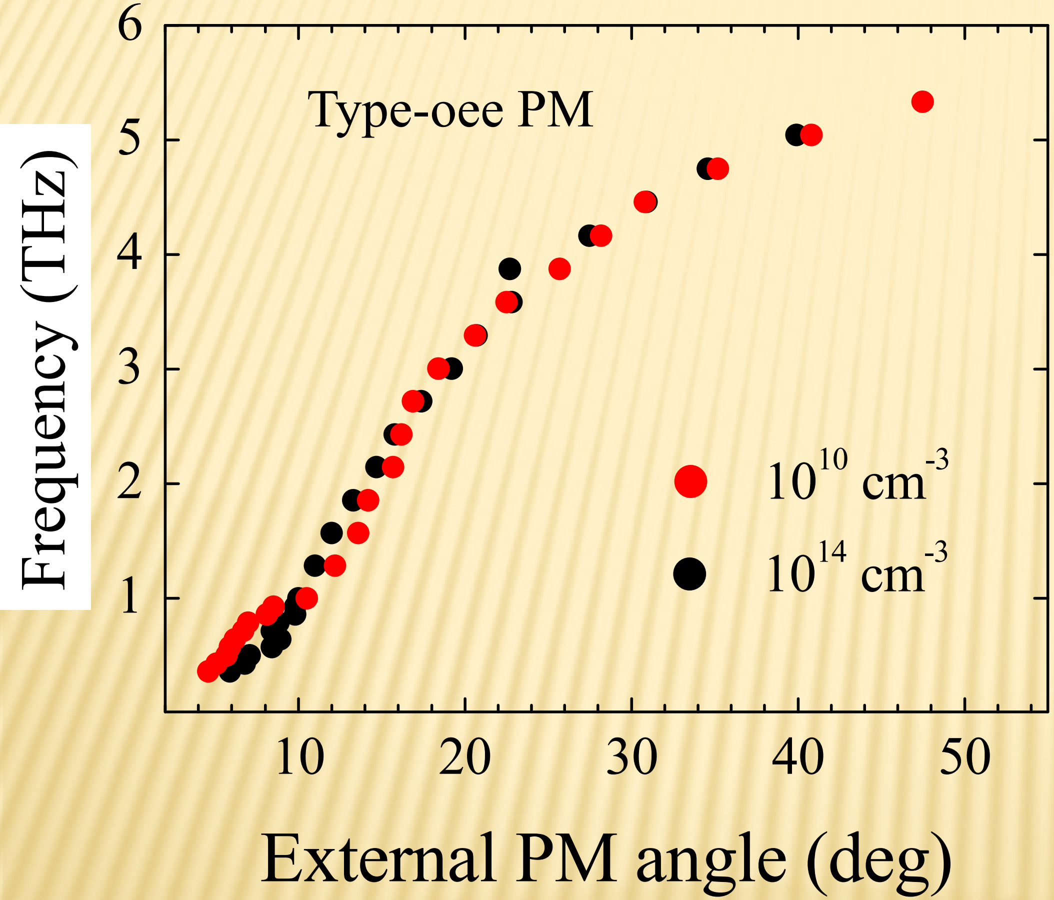
GaSe crystal grown by CVP-TDM → Improved absorption coefficient in THz frequency region

Experimental setup for THz generation

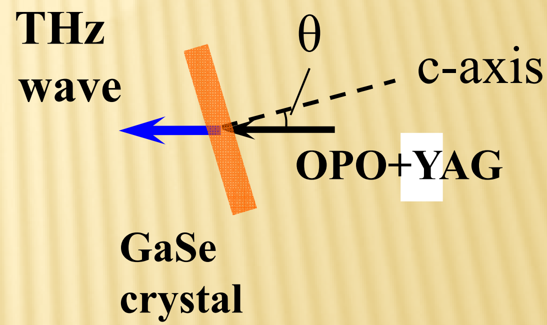


・sample： undoped-GaSe(001)： thickness of 2 mm
・beams： pump：OPO（optical parametric oscillator）
λ:1042nm－1064nm、power ～3mJ、linewidth 6GHz、pulse duration 6ns
signal：Nd:YAG laser
λ: 1064.2nm、power ～3mJ、linewidth 90MHz、pulse duration 11ns
・detector： 4K-Si bolometer

Phase matching condition



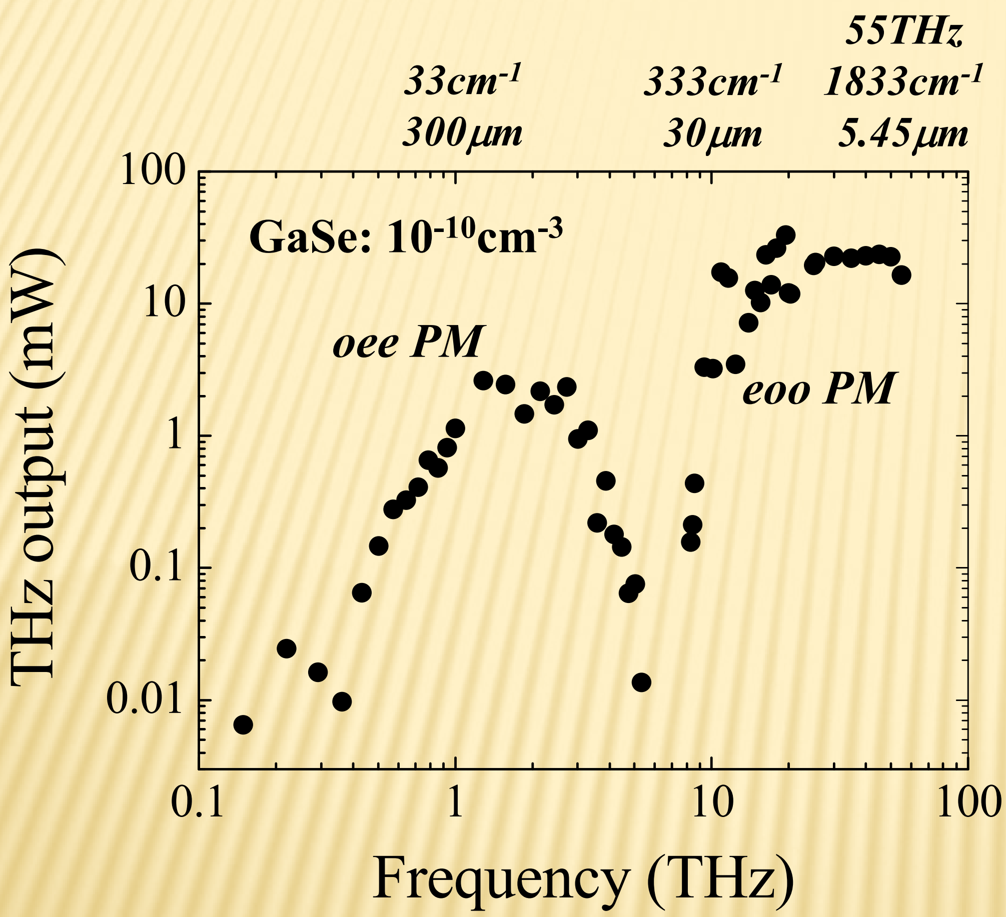
The PM angle is difference from each other at the frequency range below 2 THz.

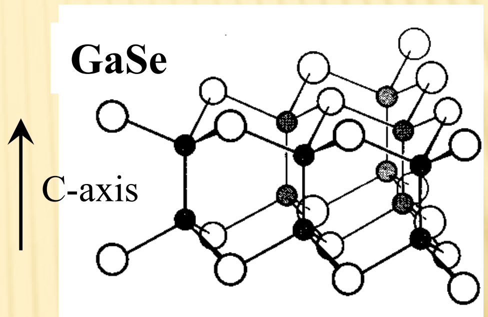


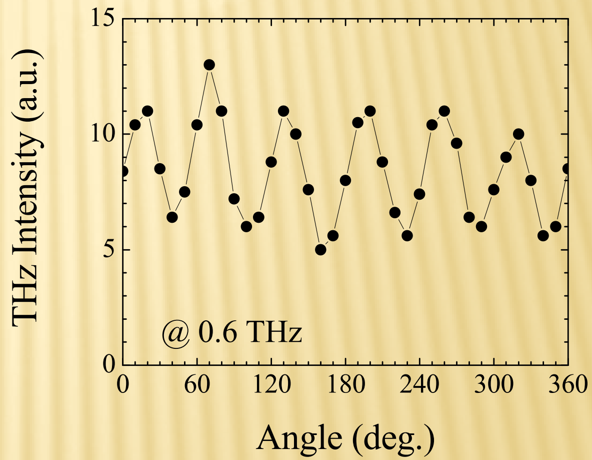
small angle tuning of two incident beams

frequency-tunable THz-wave generation

THz-generation: wave output power





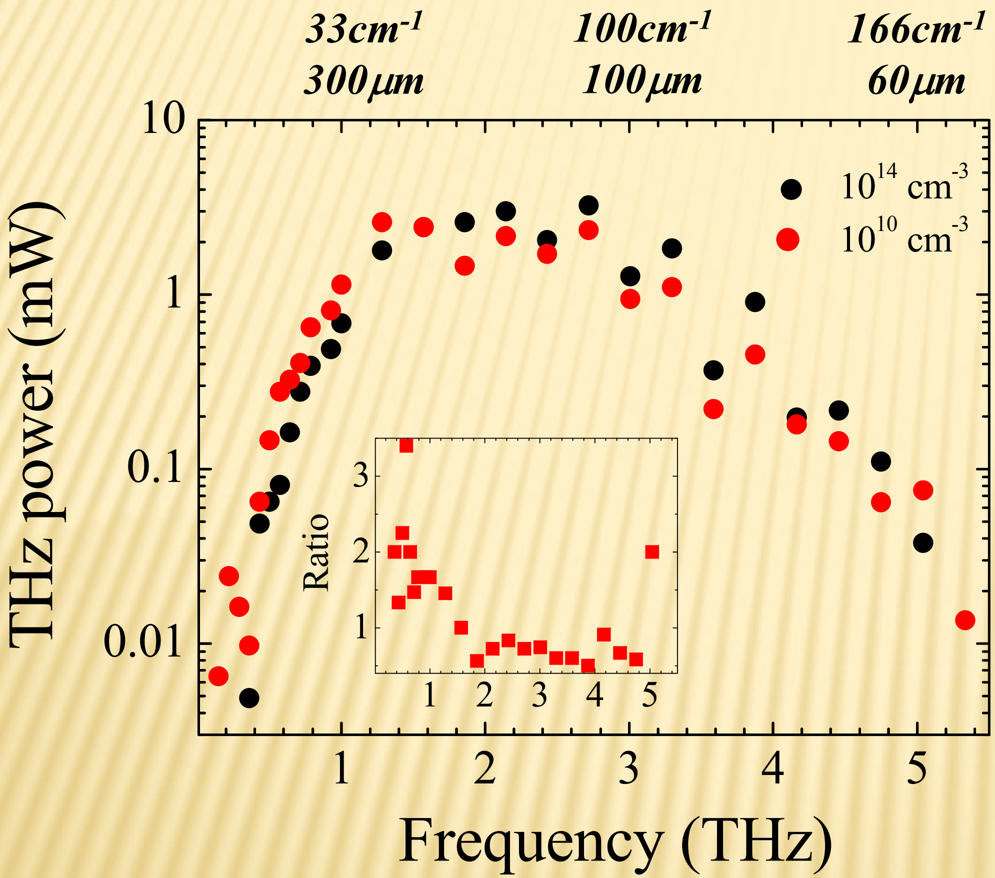


For type-*oee* collinear phase-matched DFG, the effective nonlinear optical efficiency depends on the PM (θ) and azimuthal (φ) angles as $d_{eff} = d_{22}\cos^2\theta\cos3\varphi$

the azimuthal angle satisfied $|\cos3\varphi| = 1$

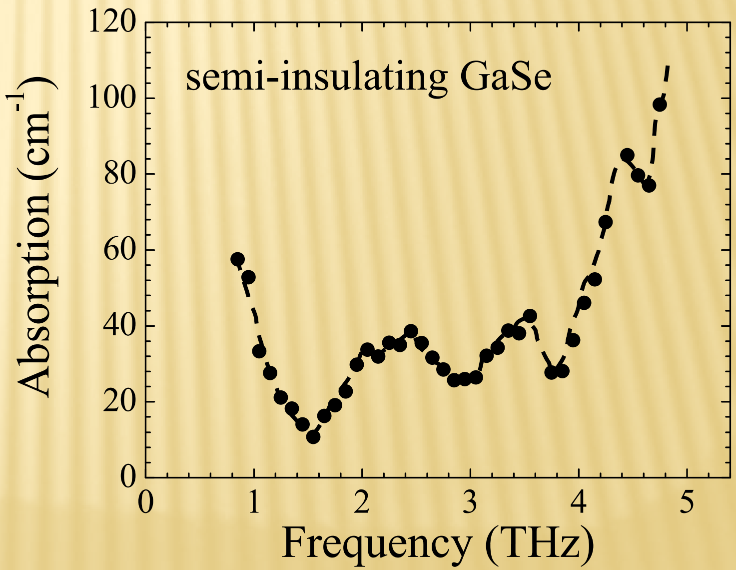
o and *e* are the ordinary and extraordinary polarization of the beams inside the crystal.

THz-wave output power in THz region



At the frequency below 1.3 THz, the pulsed THz-wave output power from the lower carrier density (10^{10} cm^{-3}) GaSe crystal was higher than that from the higher carrier density (10^{14} cm^{-3}) crystal.

The reason for the THz-wave power decrease due to free carrior absorption



In the frequency below 1 THz, the absorption coefficient increased steeply, this may be due to free carrier absorption.*

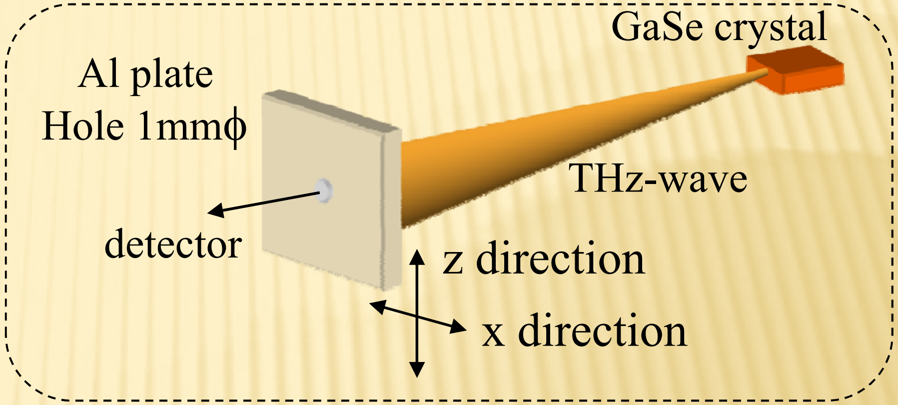
Characteristics of generated THz-waves

- **Spatial distribution of THz-waves**

  Shifting the detector with φ2 mm

  resolution: 0.25 mm

  distance: 28 cm、58 cm



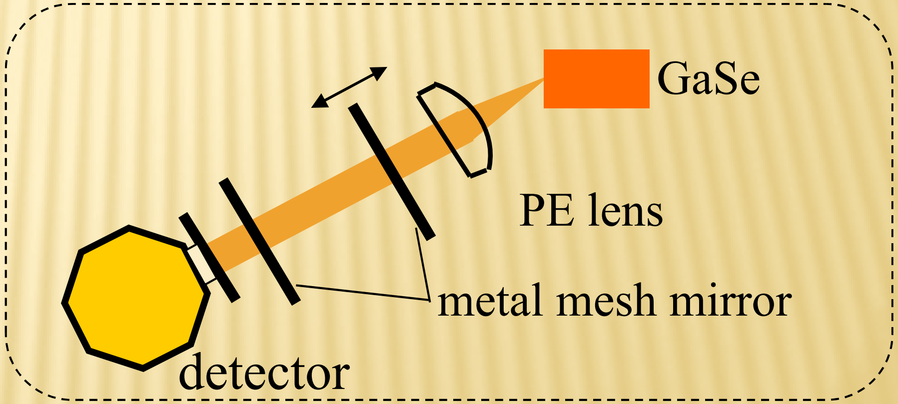
- **The-wave linewidth measurement**

  (measured frequency : 1.765 THz)

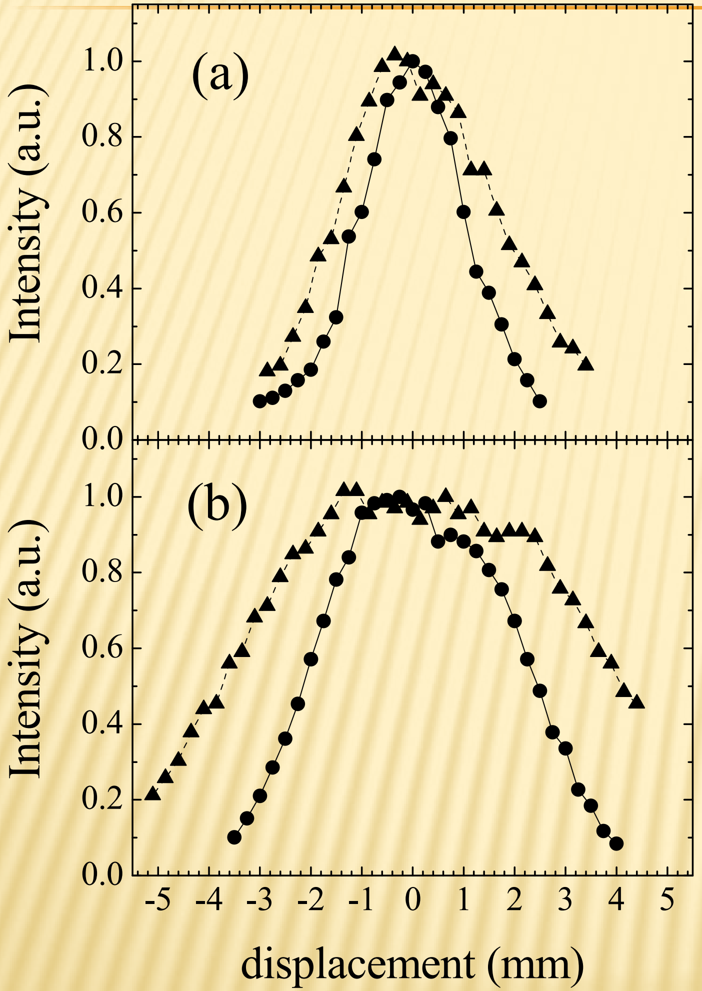
  Fabry-Perot interferometer

  high reflection metal mesh mirror

  R=97%(at 1THz)



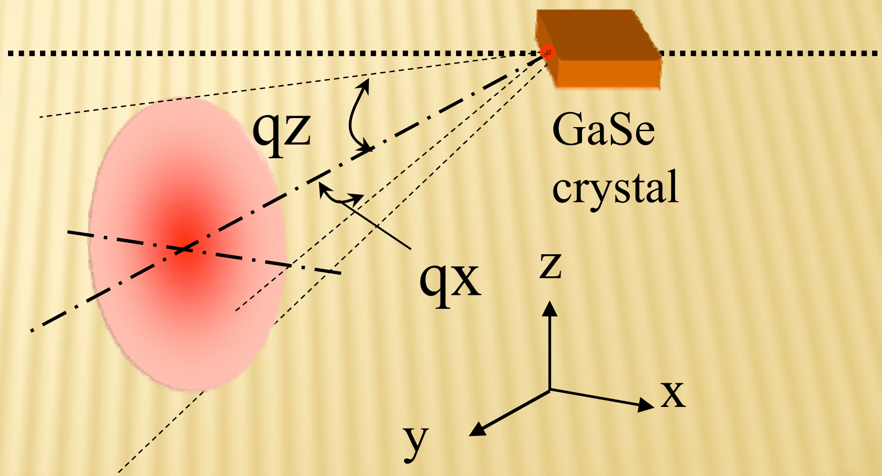
Spatial distribution of the THz-wave



THz-wave elliptically propagates from the GaSe

qx = 2.1°

qz = 3.7°

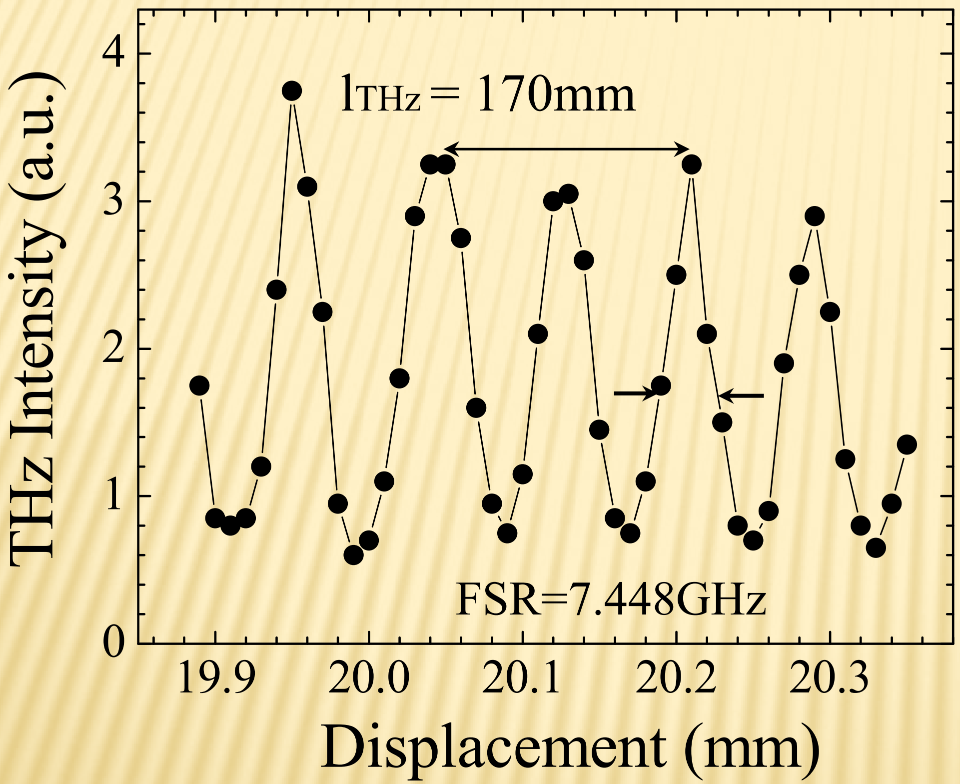


● : X-direction、▲ : Y-direction

The distance between the GaSe crystal is 28 cm (a) and 58 cm (b).

Frequency and Linewidth

Fabry-Perot interferometer



linewidth of THz-wave

3.5 GHz(0.12 cm^{-1})

suitable for source on spectral measurement with high resolution

CONCLUSION

- ε-type monocrystalline GaSe crystal growth by TDM-CVP
- Improved optical aspects in NIR & THz-frequency region (stoichiometry control via Se vapor pressure application)
- Successful coherent THz generation via DFG with collinear phase matching

↓

Defect free NLO crystal (GaSe) via stoichiometry control

For high power & wide frequency tunable THz source

Report: submission deadline 8/Sep. 2010

to oyama@material.tohoku.ac.jp by PDF format.

Read journal paper on "sophisticated laser or mm-wave–related device, materials, phenomena and/or processing"

(published in 2010), and then prepare report on that article.

At shortest 1-page your own opinion on article should be included in your report.

CONCLUSION

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