Advanced crystal growth for the development of new optical and electrical materials

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Recently, the development of new crystal materials for optical applications has become a focus of considerable interest because of the progress of optoelectronic technologies. We have carried out investigations focussing on the development of new optical and electrical materials, by systematic investigations of advanced crystal growth techniques. Here, research and progress in development of new materials and crystal growth techniques is reviewed.

1. New materials

A Nd:YVO_4 single crystal is the candidate for an LD pumped solid state laser. However, difficulty in growing sizable crystals of high optical quality has limited their industrialization. To solve this difficulty, the modified Czochralski (CZ) method has been developed. We have successfully grown a Nd:YVO_4 single crystal and even a new crystal material, $GdVO_4$, with high quality by the modified CZ method. Fig. 1 shows an as-grown Nd:$GdVO_4$ single crystal pulled at a rate of 2mm/h. Since the laser performance of Nd:$GdVO_4$, such as slope efficiency, output power and threshold pump power, has exceeded that of Nd:YVO_4, Nd:$GdVO_4$ is expected to be a promising candidate for an LD pumped solid state laser.

Recent progress of electronic technology requires new piezoelectric crystals having superior properties such as zero temperature coefficients and large electromechanical coupling factors. Although $La_3Ga_5SiO_{14}$ (LGS) is a leading candidate to satisfy those requirements, there are few reports concerning the crystal growth and the precise piezoelectric properties. We have successfully grown LGS single crystals with dimensions of 2 inches in diameter by the CZ method. Fig.2

shows an as-grown LGS single crystal pulled at a rate of 1mm/h. Grown LGS single crystals showed superior piezoelectric properties. By aliovalent substitution, a new piezoelectric material $La_3Ga_{5.5}Nb_{0.5}O_{14}$ (LGN) was developed. Under the same growth conditions as for LGS, an LGN single crystal was also successfully grown. LGN showed slightly favorable piezoelectric properties to those of LGS. LGS and LGN single crystals are superior materials for piezoelectric devices and we could expect to realize a small-sized wide band filter with lower insertion loss.

2. Advanced crystal growth

In micro single crystals with diameters below 1 mm, a low defect density can be expected. We have developed a micro-pulling down (μ-PD) method by modifying the micro-CZ method. This enables the growth of fiber shape oxide and semiconductor crystals. $K_3Li_2Nb_5O_{15}$ (KLN) and $LiNbO_3$ (LN) micro crystals without cracks and with homogeneous composition along a growth axis, have been successfully grown (Fig.3). Since incongruently melting materials such as KLN could be grown from melt with high growth rate, μ-PD method is a promising growth technique. KLN micro crystals showed strong blue light emission based on those superior non-linear optical properties. The precise control of growth atmosphere let us succeed also in growing Si and Si-Ge fiber crystals with dimensions of 200 μm in diameter.

Numerous efforts have been made to realize the growth of LN thin film single crystals with high quality. Solid-liquid coexisting liquid phase epitaxy (LPE) brought us success in growing high quality LN thin film single crystals with dimensions of 3 inches in diameter on the LN substrate for optical waveguide applications (Fig.4). The quality of grown film crystals was higher than that of optical grade of LN substrate. Wide range variation of thickness and composition of grown thin film LN crystals was also valid by solid-liquid coexisting LPE method.

Er^{3+} doped CaF_2 thin film crystals have been successfully grown on the substrate of CaF_2 single crystals (Fig.5), by molecular beam epitaxy (MBE). While the MBE method has been used for the growth of semiconductor materials, this method was found to be applicable to the growth of oxide and fluoride materials. Green light emission was observed from the grown $Er:CaF_2$ thin film by the up-conversion process of energy levels in Er^{3+}. A series of rare-earth fluoride thin film crystals are expected to be grown and extended in their application range by the MBE method.

Although a ZnSe single crystal is one of the most promising materials for the blue light laser, the difficulty of its growth has still limited industrialization. Twinning phenomena were the faults of its growth. Using polycrystals as a seed crystal, we have successfully grown ZnSe bulk single crystals with drastically reduced twin density by the vertical Bridgman method. (100) substrates suitable for homoepitaxial growth could be cut off from grown crystals (Fig.6).

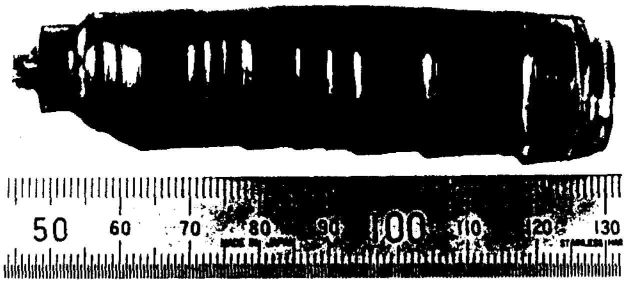

Fig. 1 As-grown Nd:$GdVO_4$ single crystal.

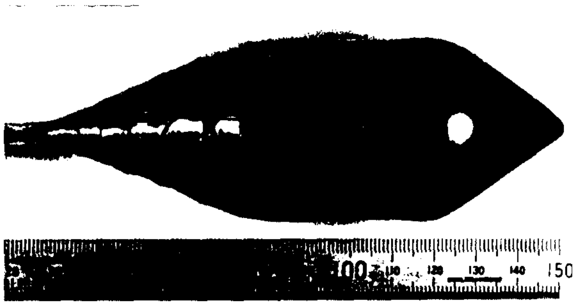

Fig. 2 As-grown $La_3Ga_5SiO_{14}$ single crystal.

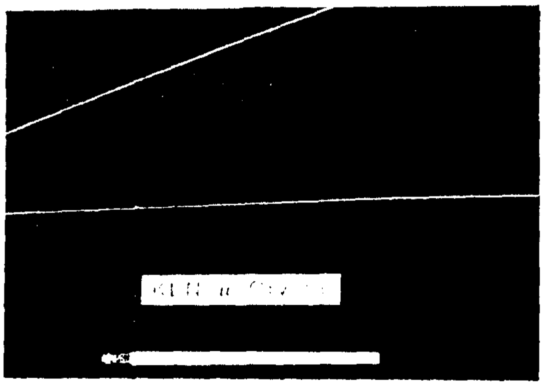

Fig.3 As-grown KLN micro crystal.

Fig.4 3-inch wafer size LN epitaxial film.

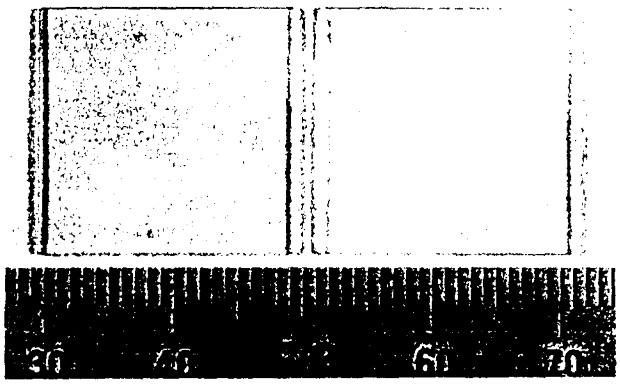

Fig.5 Er:CaF_2 thin film crystal on CaF_2 substrate.

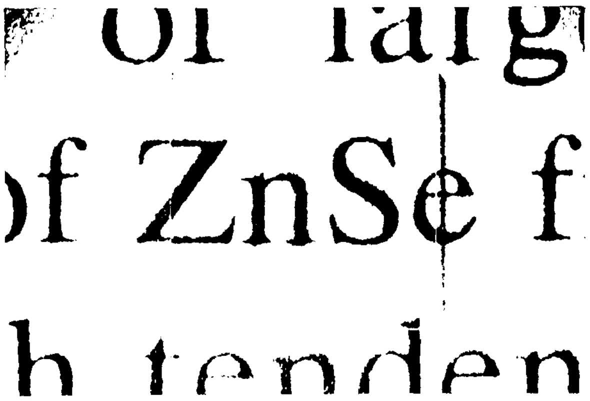

Fig.6 Polished (100) ZnSe wafer.

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Tsuguo Fukuda

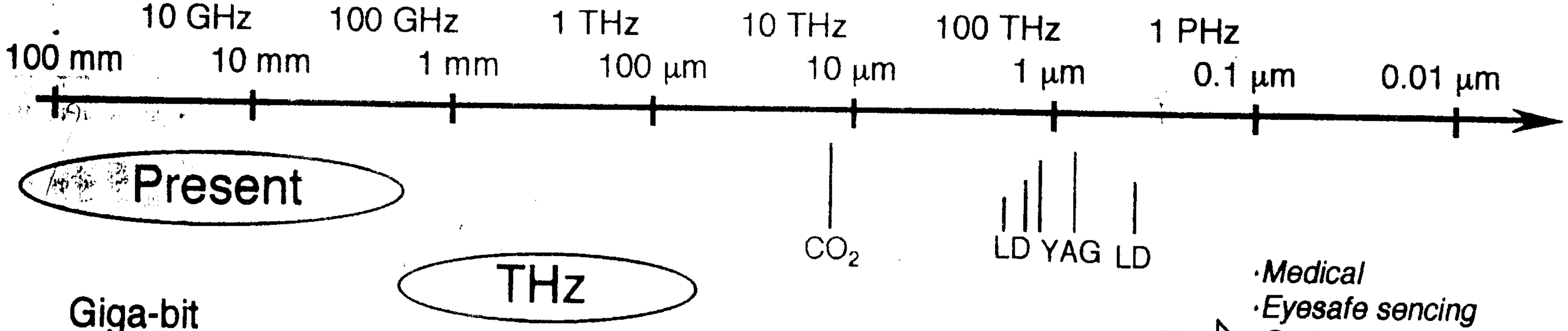
Institute for Materials Research, Tohoku University

Photonics Applications

Spectrum Frontier

Single crystals
Advanced crystal growth

Wave length (Frequency) Exploitation



Giga-bit
Si Technology

Si : MCZ

Wide pass band
Langasite : CZ

Not exploited as
electromagnetic wave

- *Medical*
- *Eyesafe sencing*
- *Optical Information*
- *Next generation*
  Optical communication

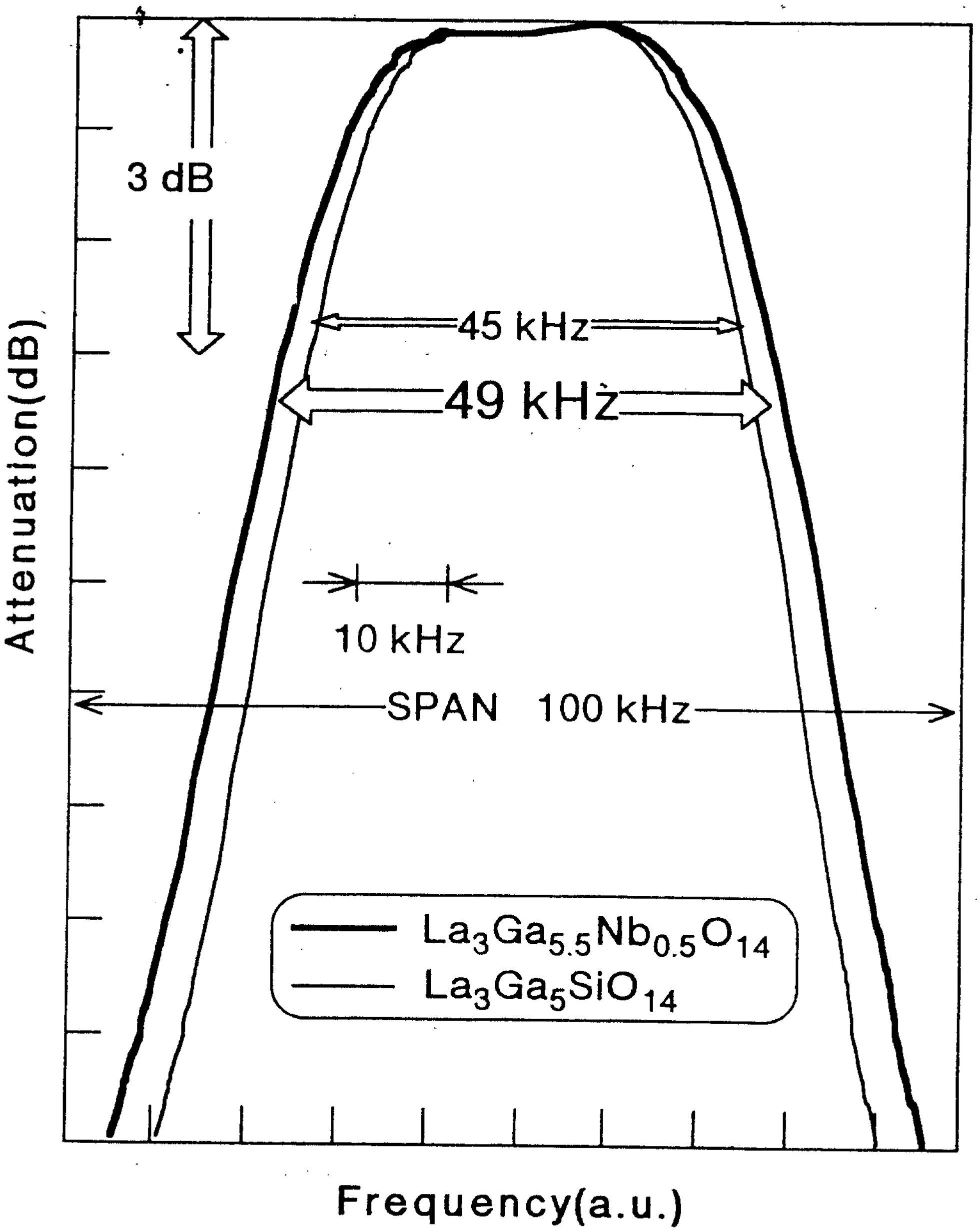
Laser
LD pumped laser technology
Nonlinear optical crystal, SHG
Up-conversion laser

Tm/CNGG, $Tm/GdVO_4$, $Yb/GdVO_4$: modified CZ
Nd/YVO_4, $Nd/GdVO_4$: modified CZ
KLN : μ-PD
$Li_2B_4O_7$* : CZ
Er/CaF_2, Er/LaF_3 : MBE

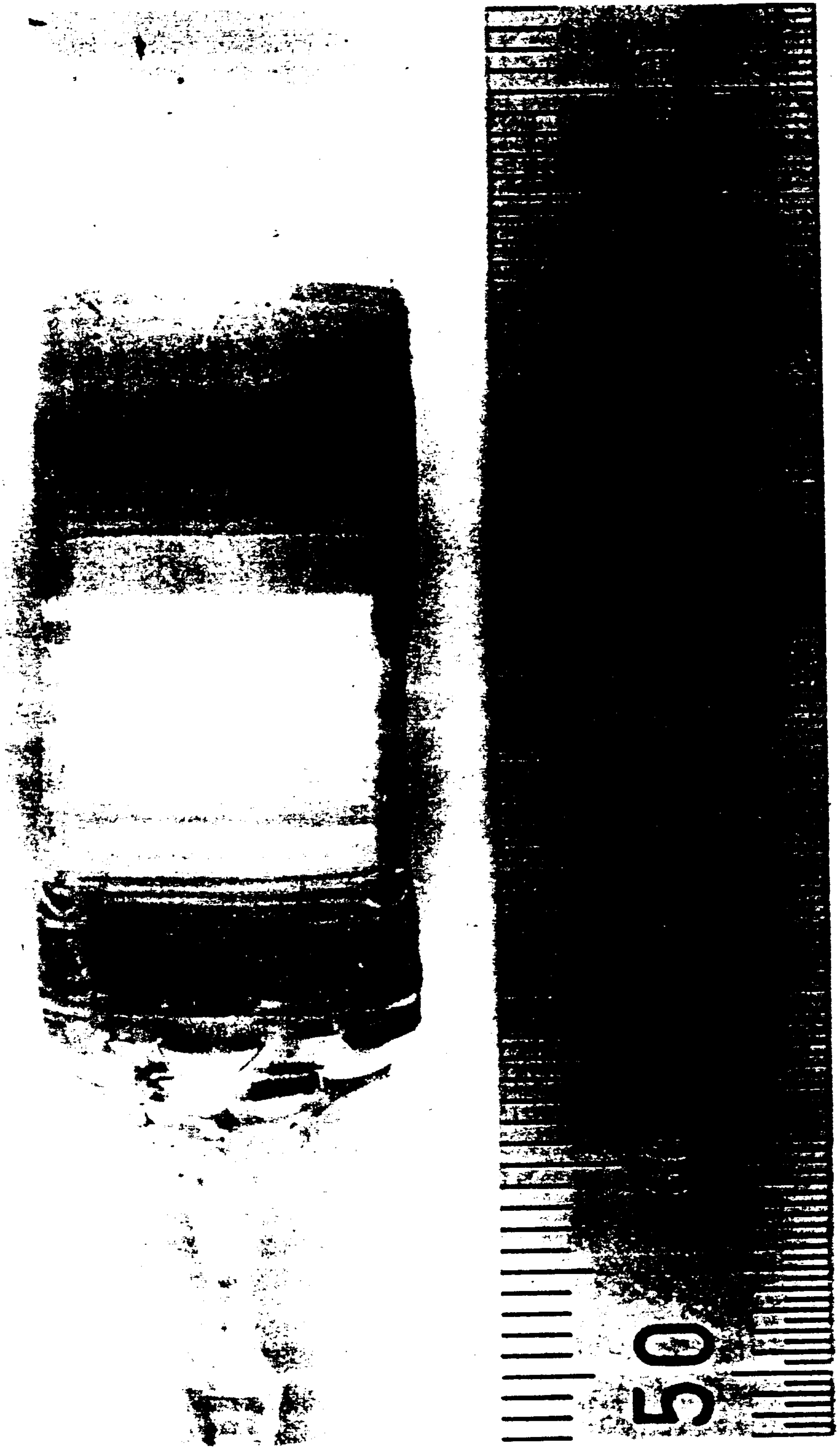
* Mitsubishi Mat. Co.,Ltd.
Dr.Uda

Comparison of properties of each crystal

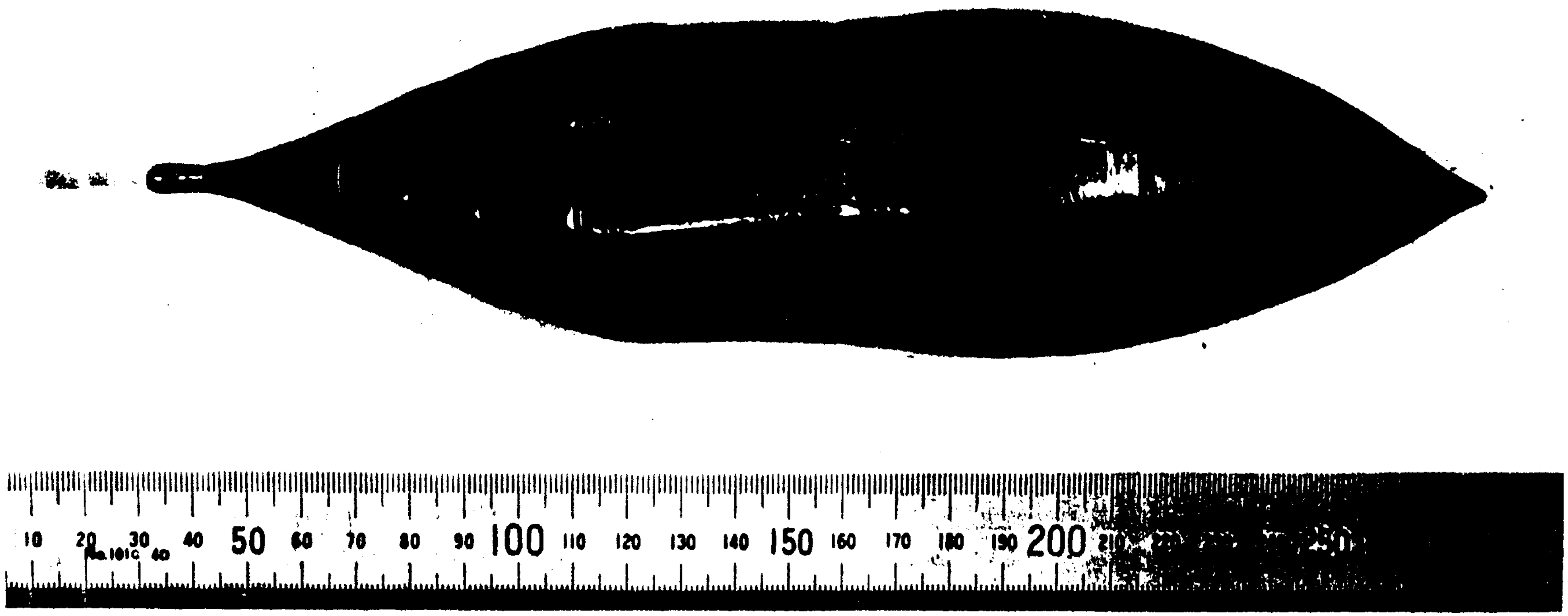
	$LiTaO_3$	$La_3Ga_5SiO_{14}$	$La_3Ga_{5.5}Nb_{0.5}O_{14}$	Quartz
phase transition	665 ℃	none	none	573 ℃
melting temp. (℃)	1650	1470	1470	——
mohs hardness	5～6	6～7	6～7	7
electro-mechanical coupling factor k [%]	43	15～25	～30	7
Q value	5000	30000～ 40000	60000～ 120000	100000～ 200000
equivalent series resistance [Ω]	——	2～5	0.7～1.7	20～40
frequency variation [ppm] (-20～70℃)	200～400	100～150	——	50～80



Pass band characteristic of $La_3Ga_5Nb_{0.5}O_{14}$ filters

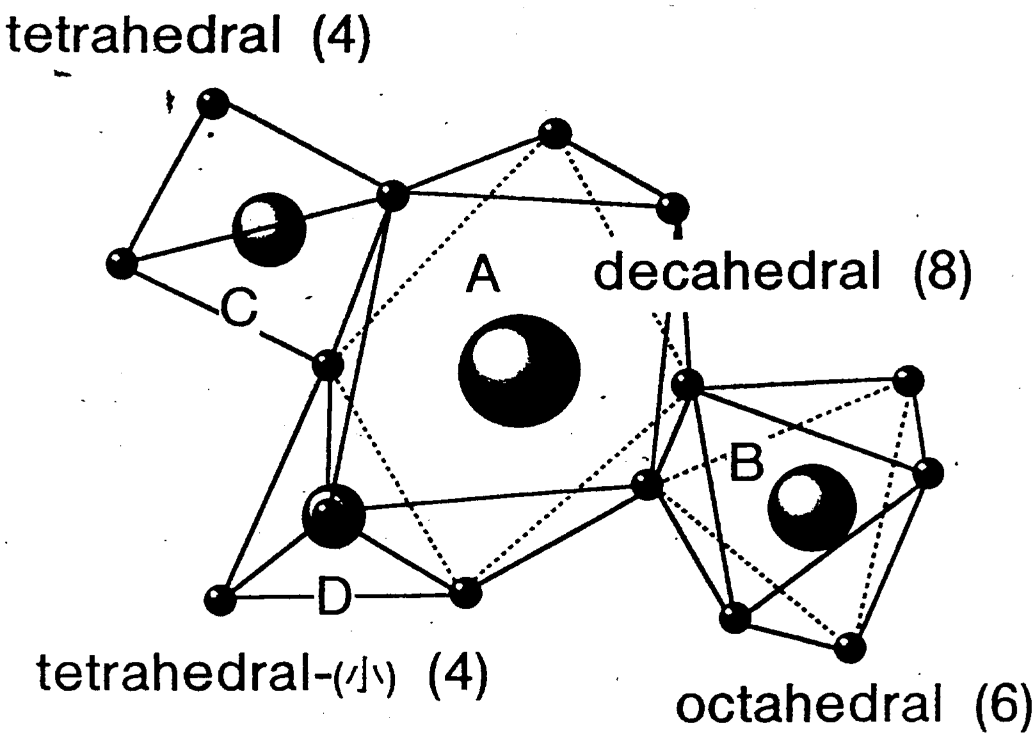


$La_3Ga_{5.5}Ta_{0.5}O_{14}$ 1 mm/h



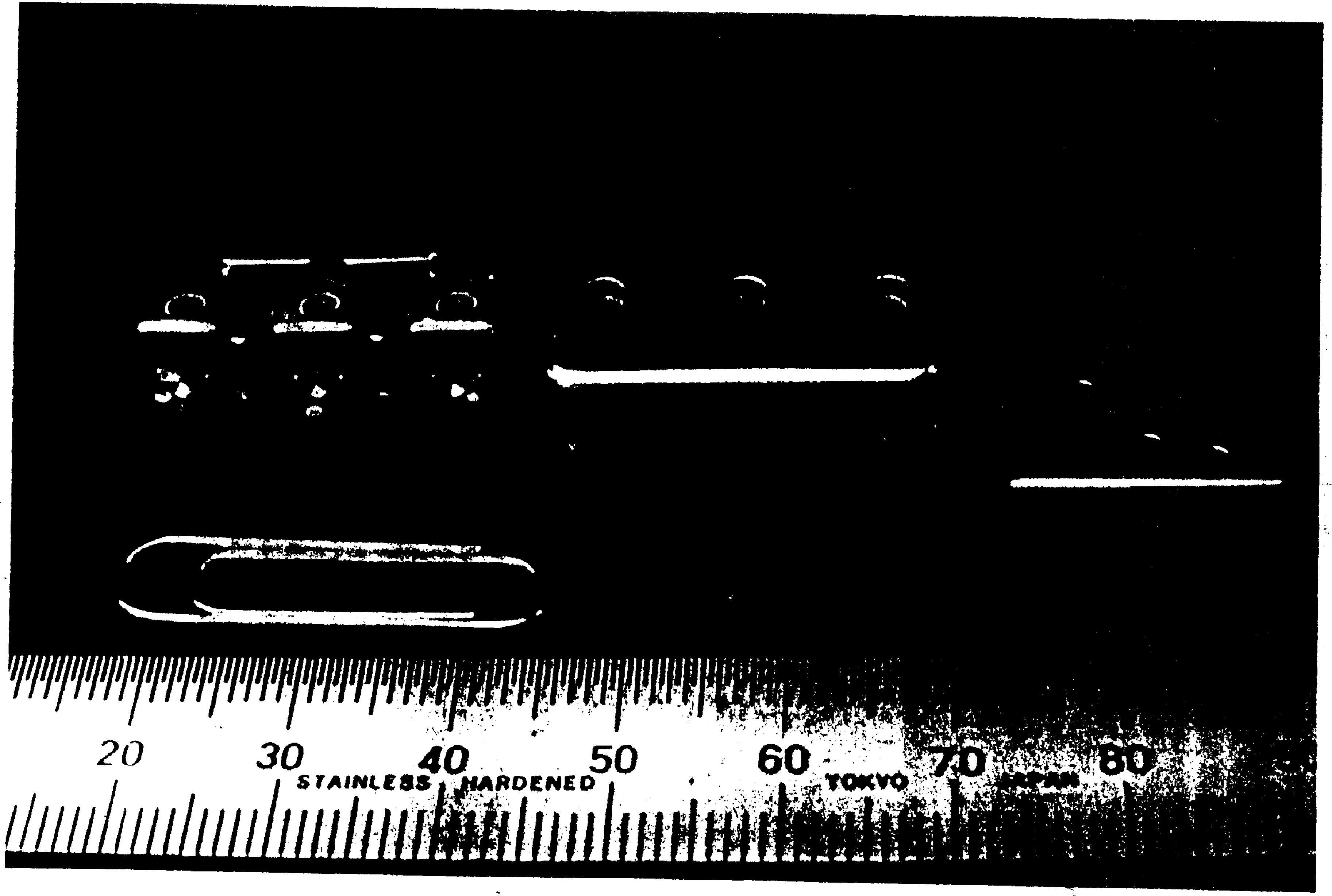
2"Ø $La_3Ga_{5.5}Nb_{0.5}O_{14}$ 1 mm/h

$A_3 B C_3 D_2 O_{14}$



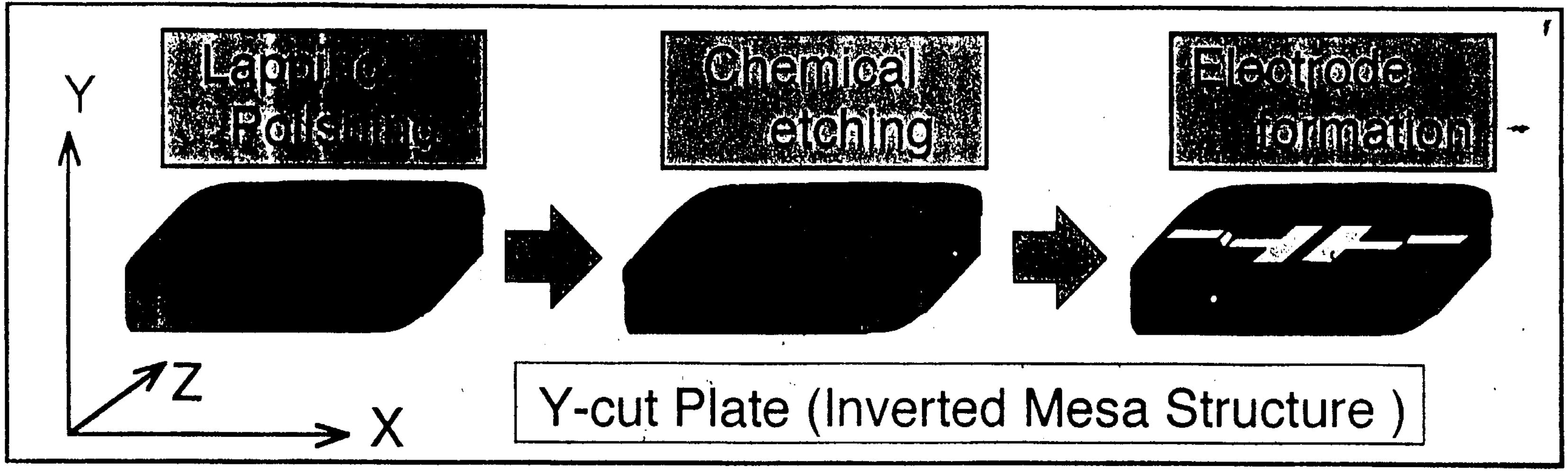
$$Si^{4+} \longrightarrow \begin{array}{l} Ga^{3+} + Nb^{5+} \\ Ga^{3+} + Ta^{5+} \end{array}$$

	$La_3Ga_5SiO_{14}$	$La_3Ga_{5.5}Nb_{0.5}O_{14}$ $La_3Ga_{5.5}Ta_{0.5}O_{14}$
A	La^{3+}	La^{3+}
B	Ga^{3+}	Ga^{3+}, Nb^{5+}, Ta^{5+}
C	Ga^{3+}	Ga^{3+}
D	Ga^{3+}, Si^{4+}	Ga^{3+}



Conventional discrete-type quartz filter
and new-type LGS filter

Structure of 71 MHz filter using $La_3Ga_5SiO_{14}$



Y-cut Plate (Inverted Mesa Structure)

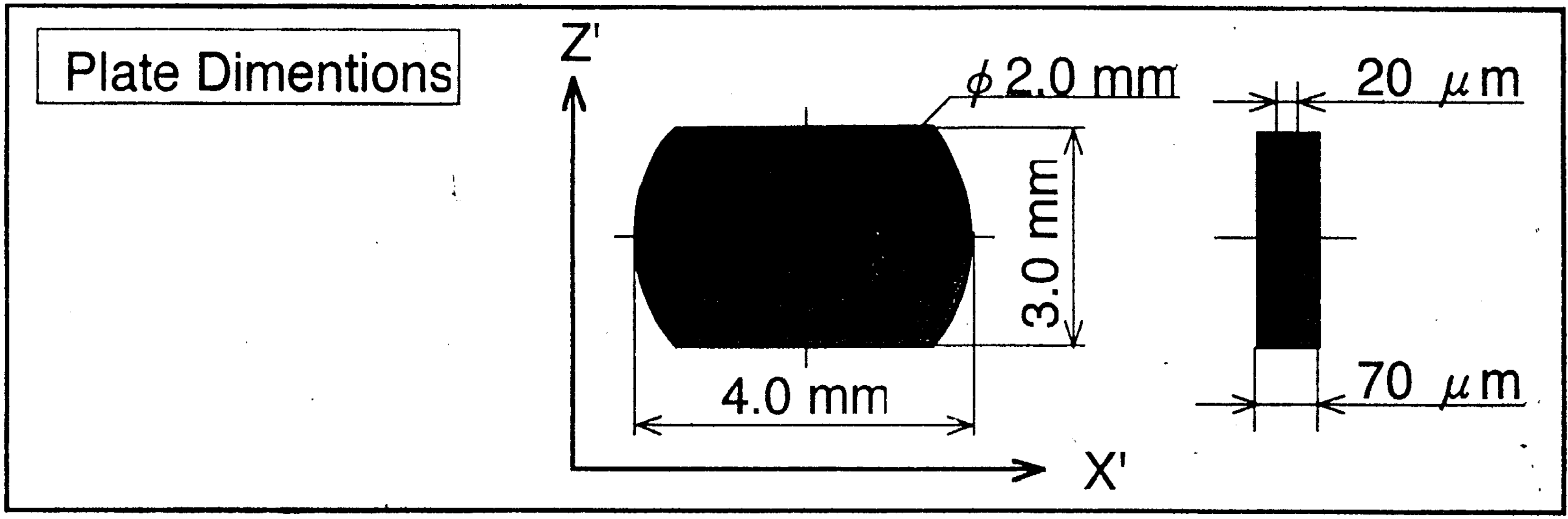
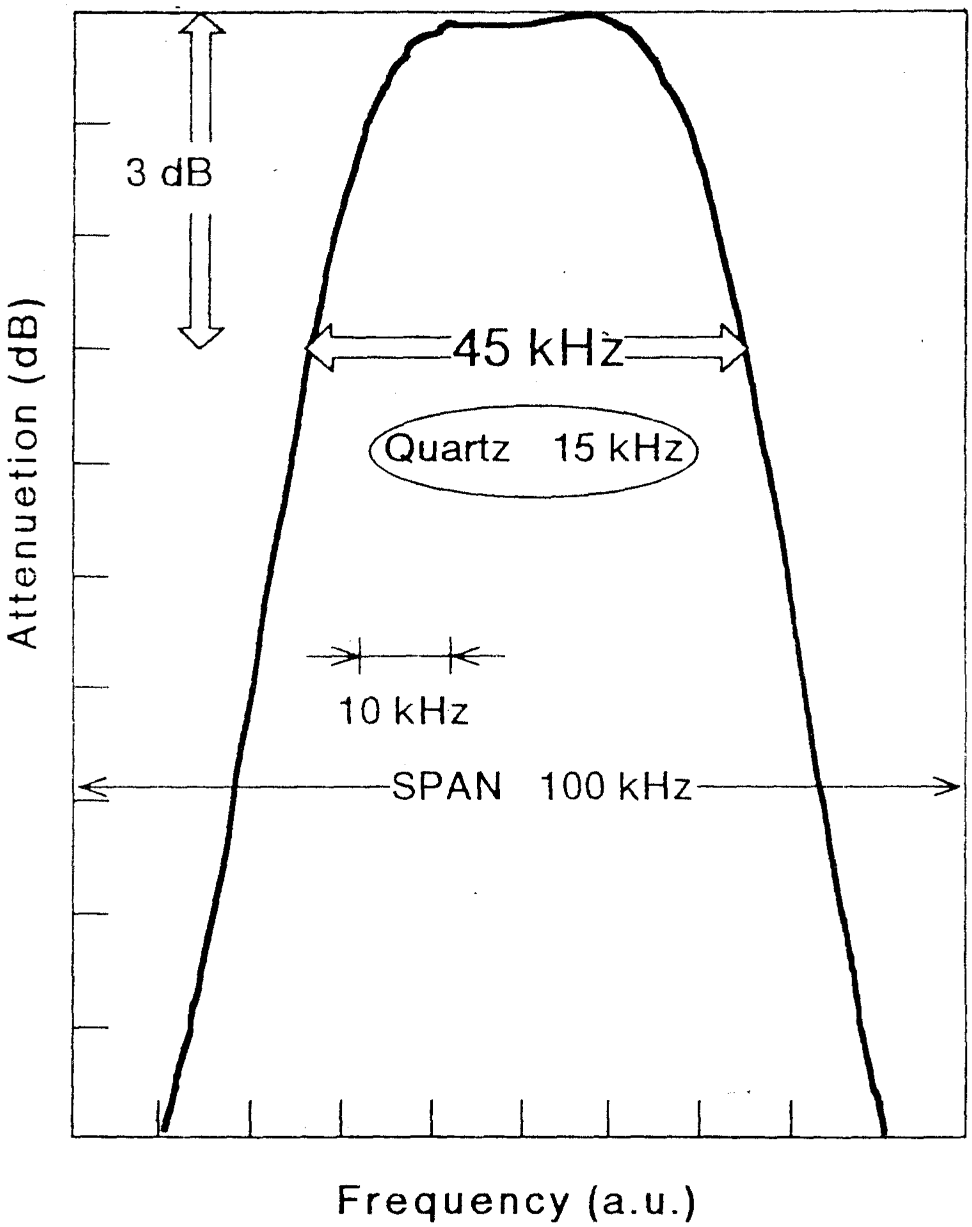
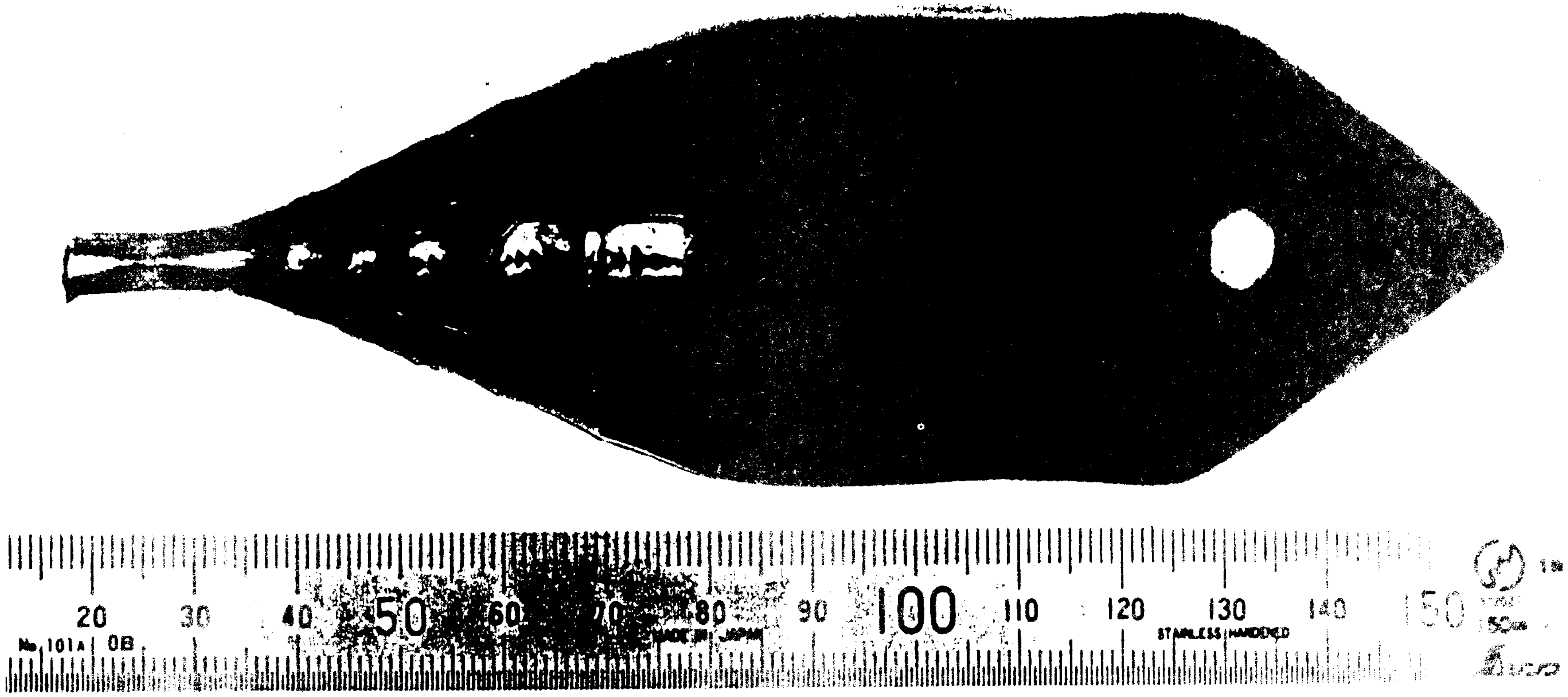


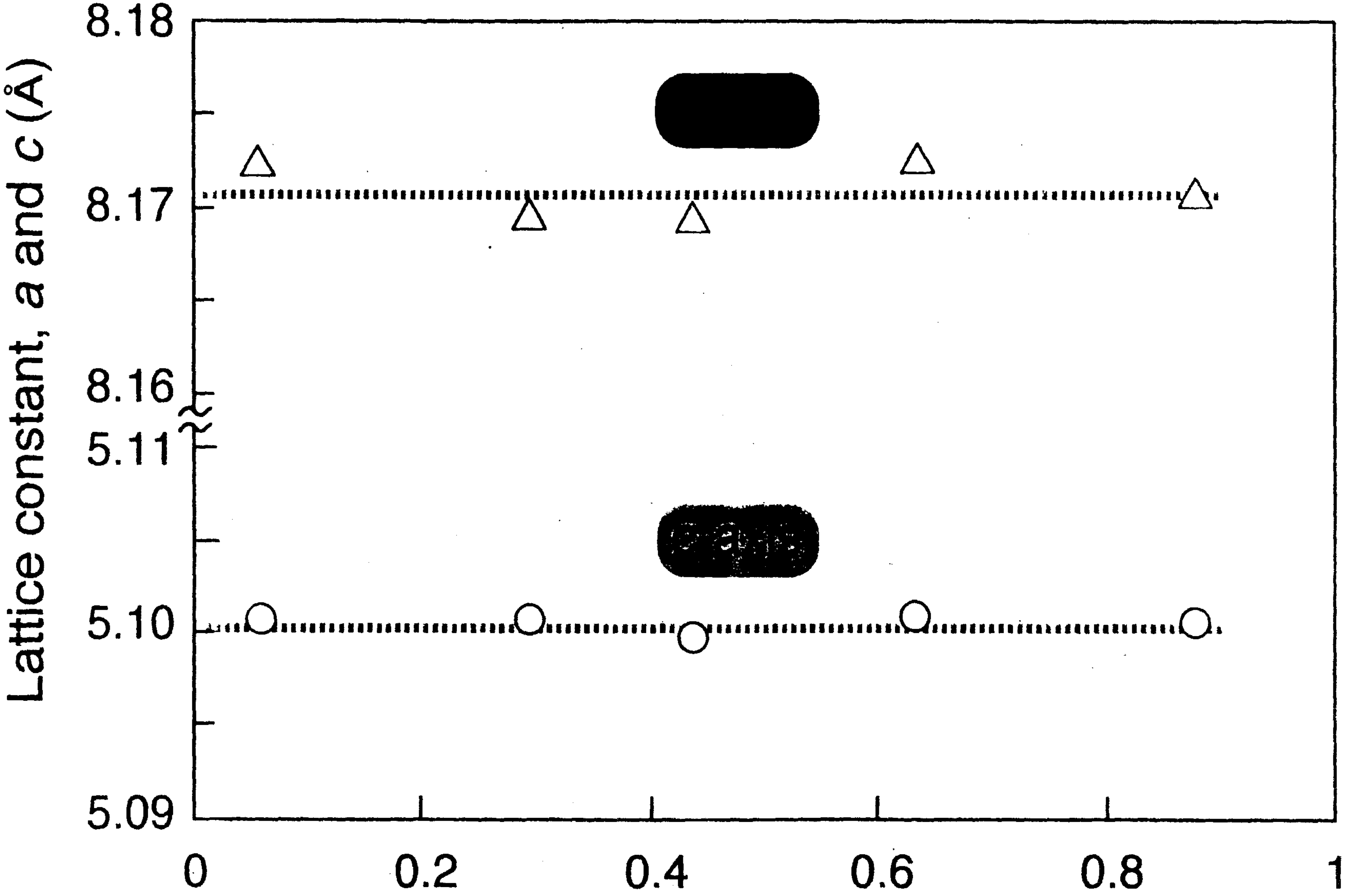
Plate Dimentions



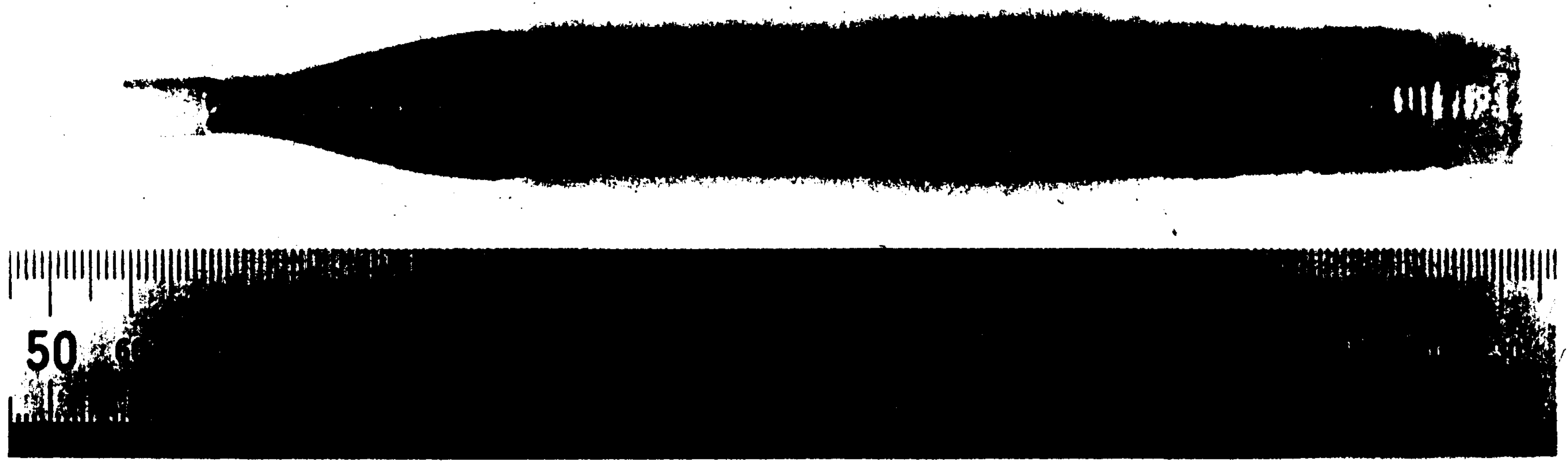
Pass band characteristic of $La_3Ga_5SiO_{14}$ filters



2"Ø $La_3Ga_5SiO_{14}$ 1 mm/h



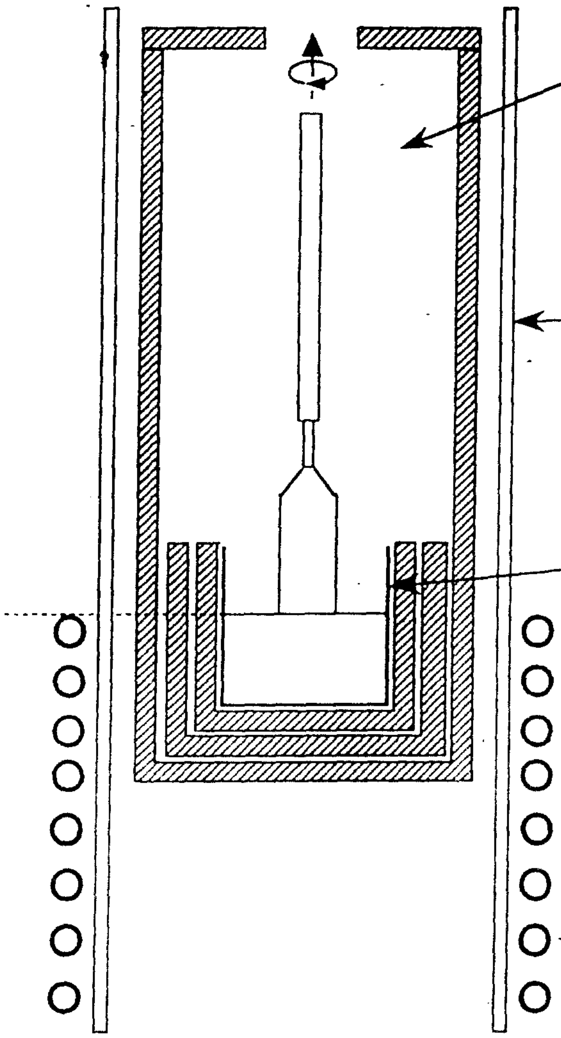
Lattice constants, *a* and *c* vs. solidification fraction, *g* of LGS



1"Ø $La_3Ga_5SiO_{14}$ 2.0 mm/h

solidification fraction ≈ 1

Experimental set-up



Ar + 1 vol%O_2

quartz tube

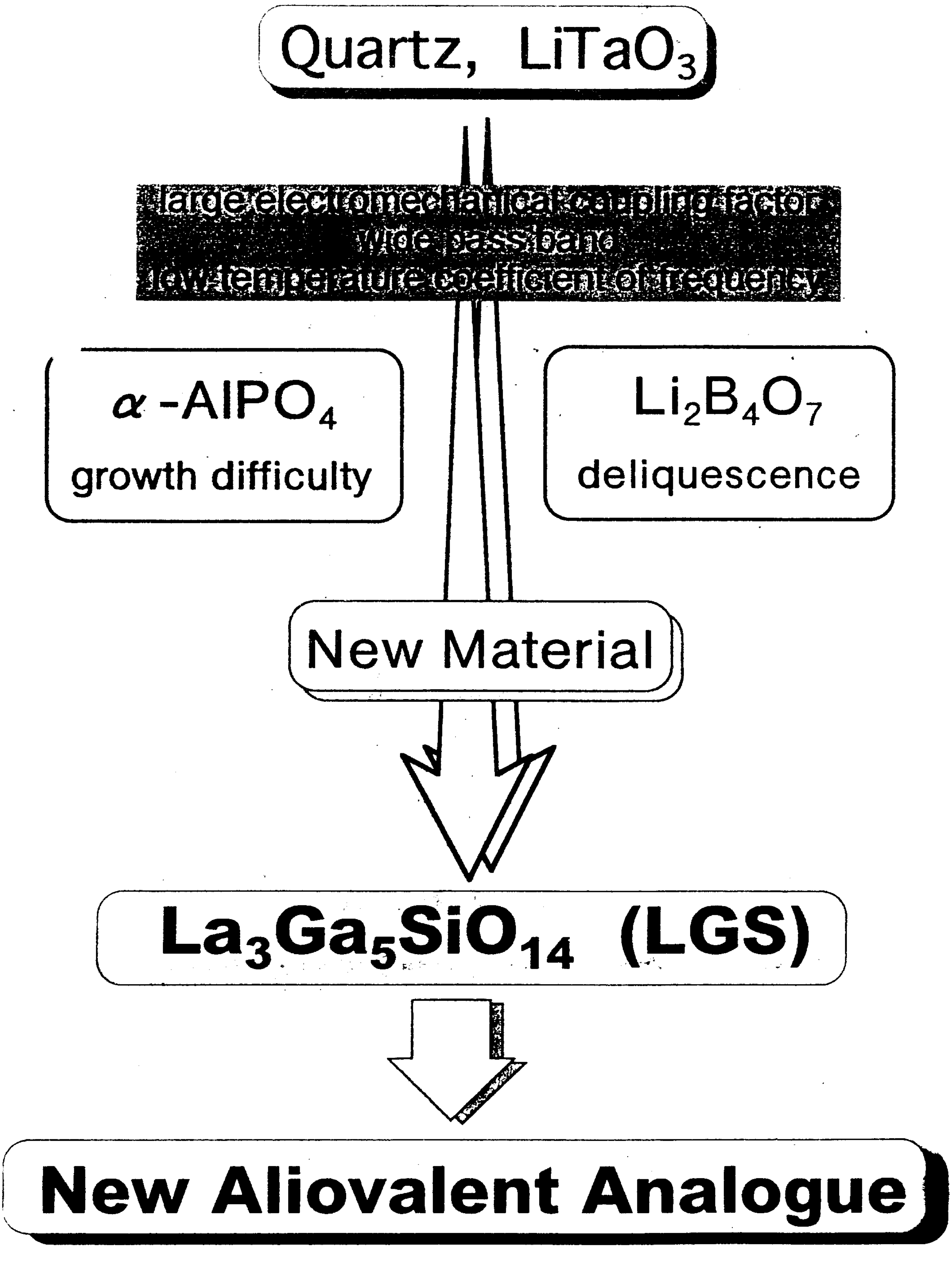
crucible
Pt, Ir, Pt/Rh

T_m = 1470 °C
congruent melting

R.F. coil

Growth conditions

- ratation rate : 10 rpm
- pulling rate : 1～3 mm/h
- starting materials : oxide powders (4N)
  stoichimetric composition



Quartz, $LiTaO_3$

large electromechanical coupling factor
wide passband
low temperature coefficient of frequency

α-$AlPO_4$
growth difficulty

$Li_2B_4O_7$
deliquescence

New Material

$La_3Ga_5SiO_{14}$ (LGS)

New Aliovalent Analogue

- Efficient Use of Frequency
- High Quality／Security
- Economical System

Digitalizing

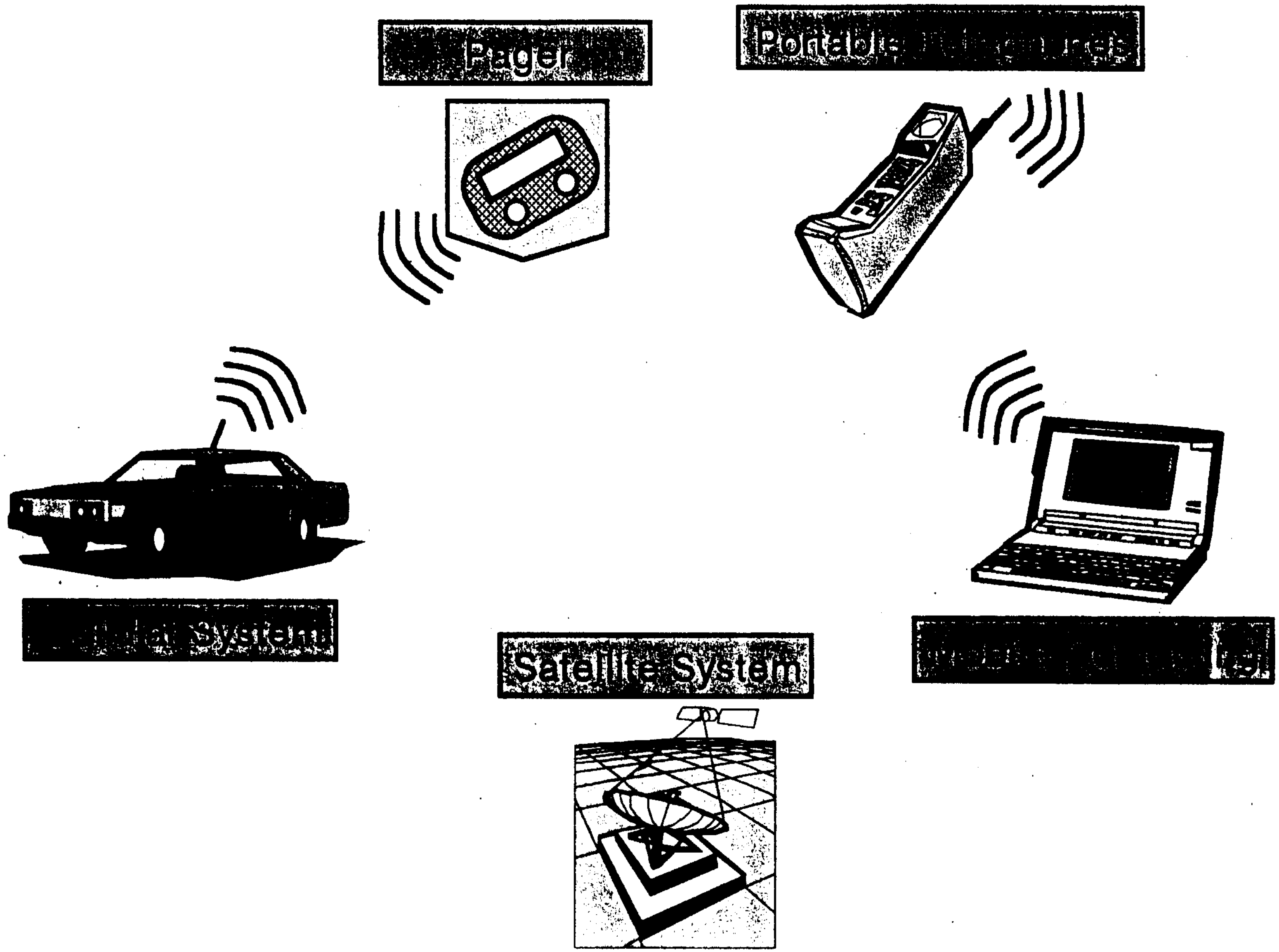
Digital Cellular System

- Japan : PDC (Personal Digital Cellular System)
- Europe : GSM (Global System for Mobile Com.)
- North America : TIA (Telecom. Industry Assn.)

Piezoelectric Components

- High Frequency
- Micromachining
- Small Loss
- Wide Pass Band

Development of Mobile Communications



Outline

1. Introduction

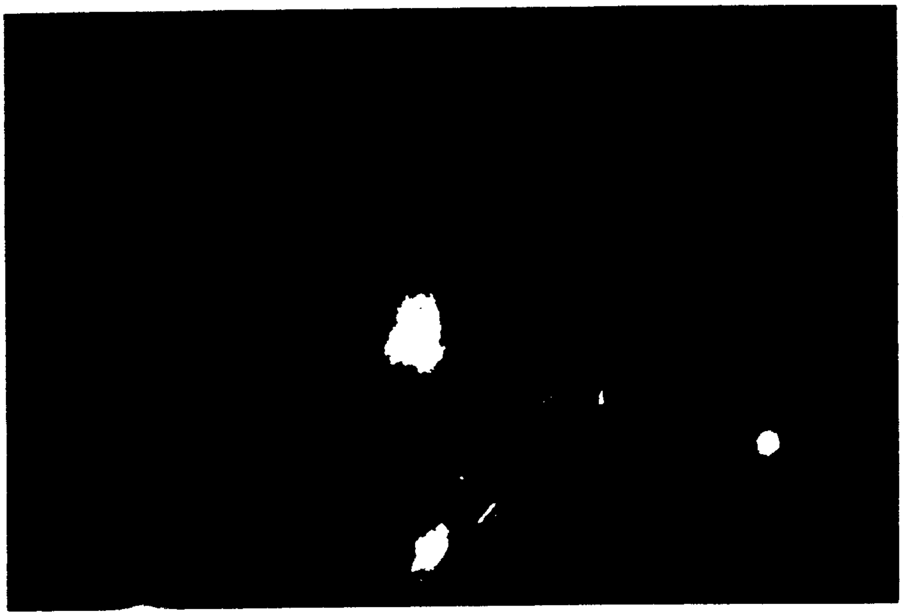
2. New Langasite type piezoelectric single crystals grown by CZ method

3. Blue SHG KLN single crystal grown by μ-PD method

4. Er : LaF_3 film crystals for up conversion laser grown by MBE method

5. Summary

Generation of blue SH laser



Fundamental ;
820 nm, 160 mW

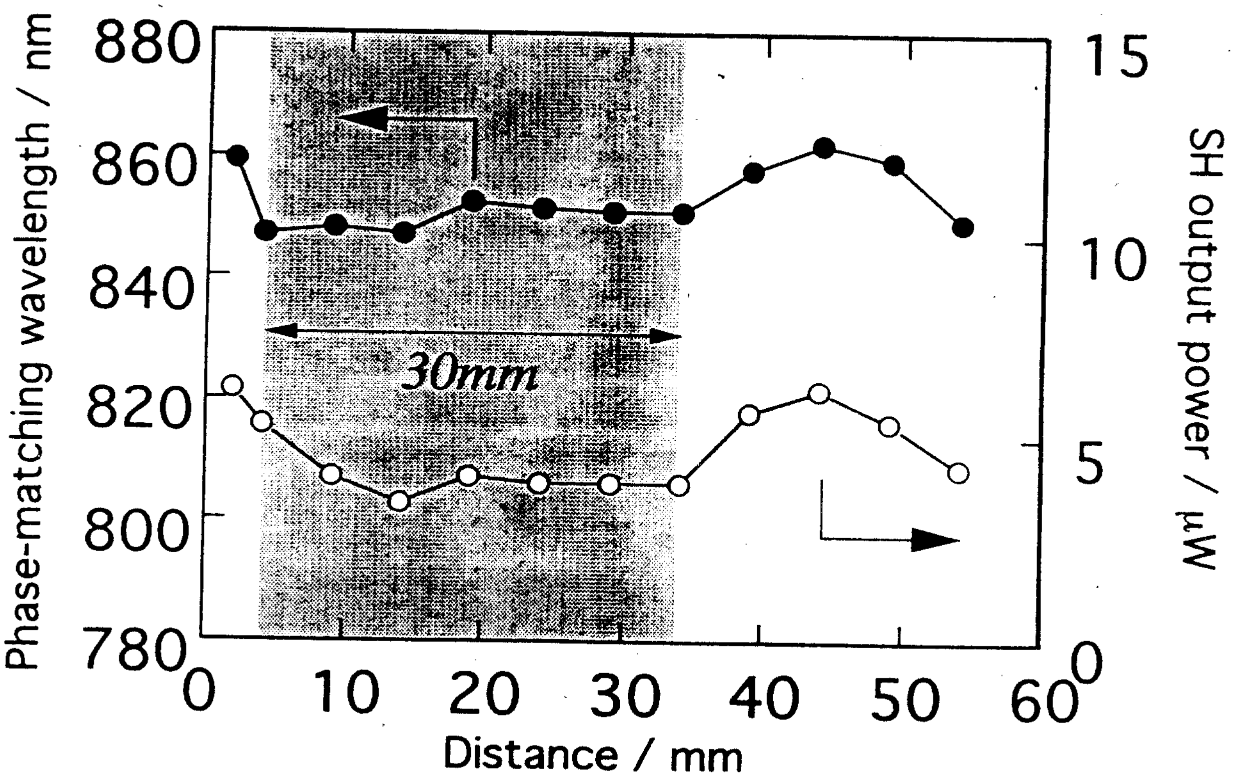
⇒

SHG ;
410 nm, 69 μW

SHG efficiency

Theoretical value : 2.08%/W
Maximum value : 0.31% /W
[=15% of theoretical value]

SHG properties along the growth axis

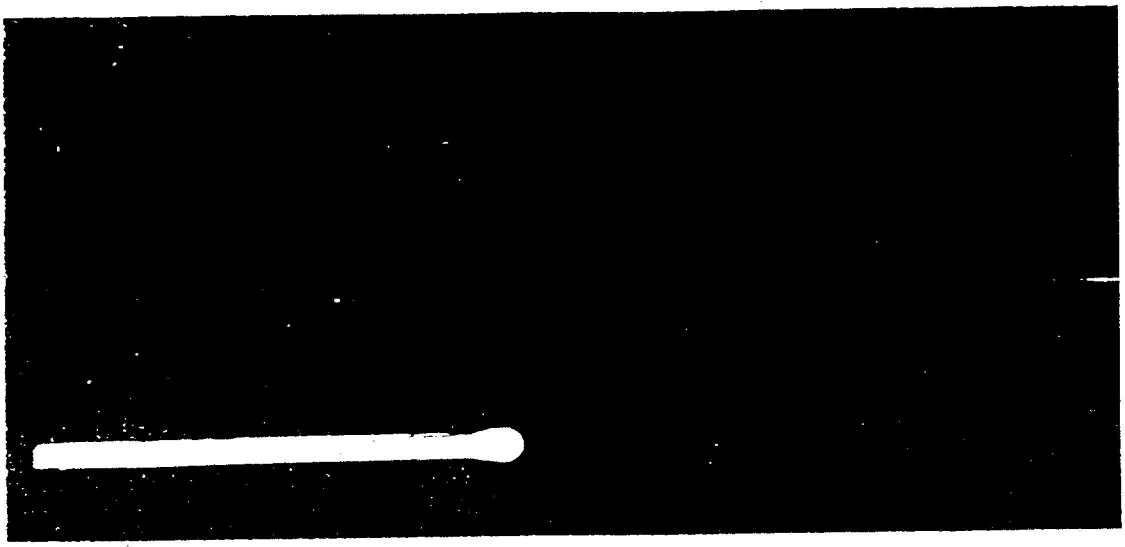


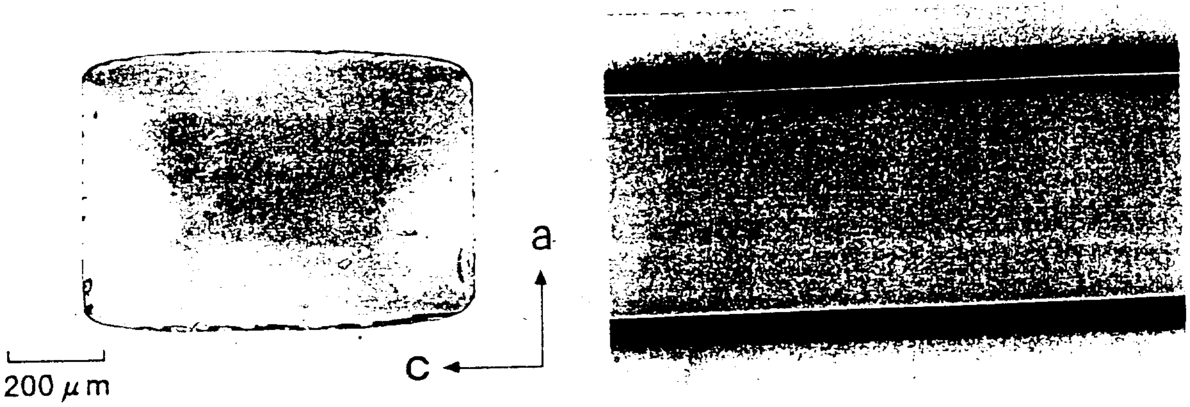
◇Deviations

Phase-matched wavelength	: ±2.6nm / 30 mm
SH output power	: ±18% / 30 mm

3. Characterization

KLN single crystal fiber





cross-section

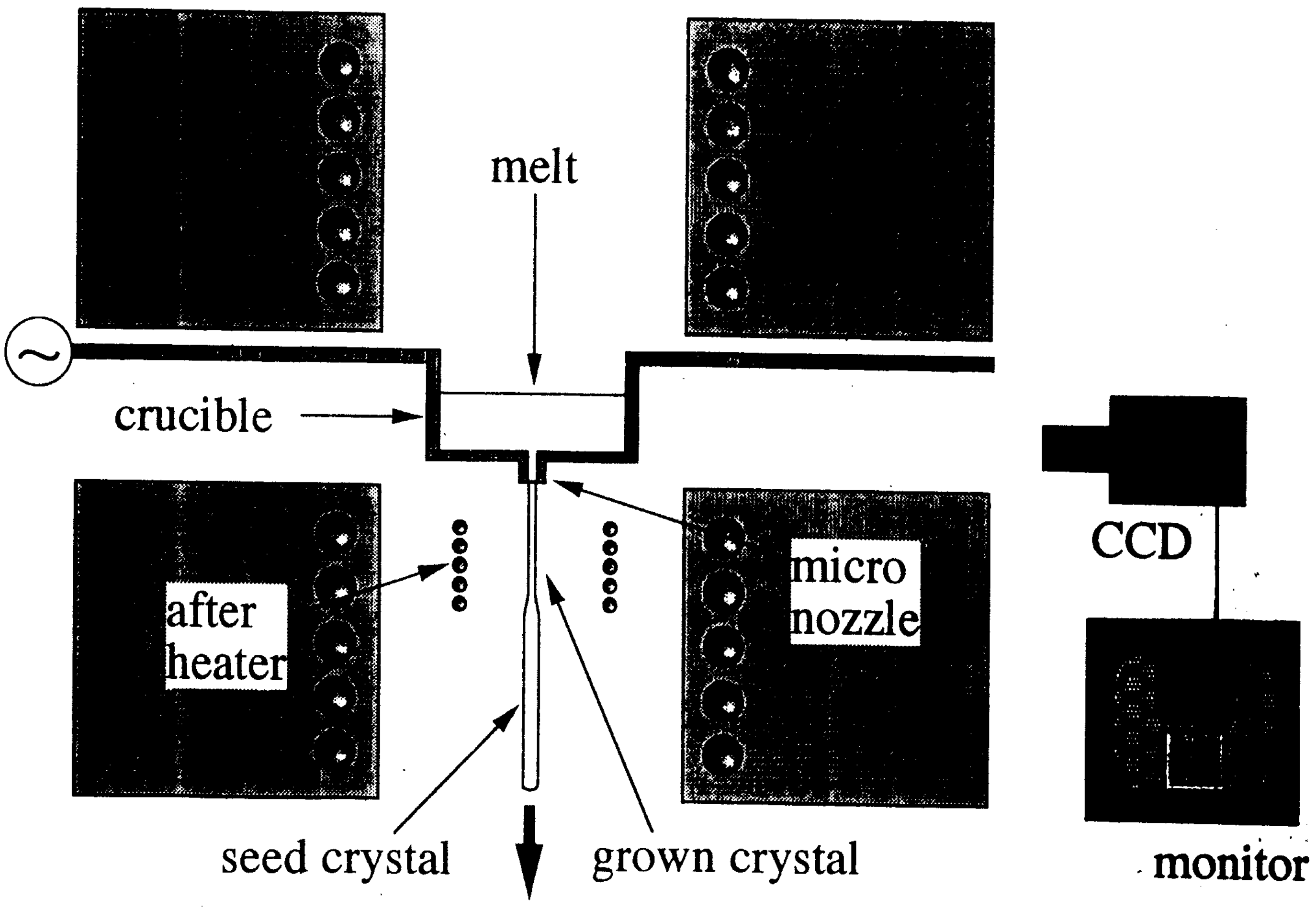
side

microscopic image

- Rectangular cross-section, □0.5-0.8mm
- Uniform diameter
- Maximum length ~300mm
- No macro defects (crack, inclusion, bubble)

2. Experimental

μ-PD apparatus

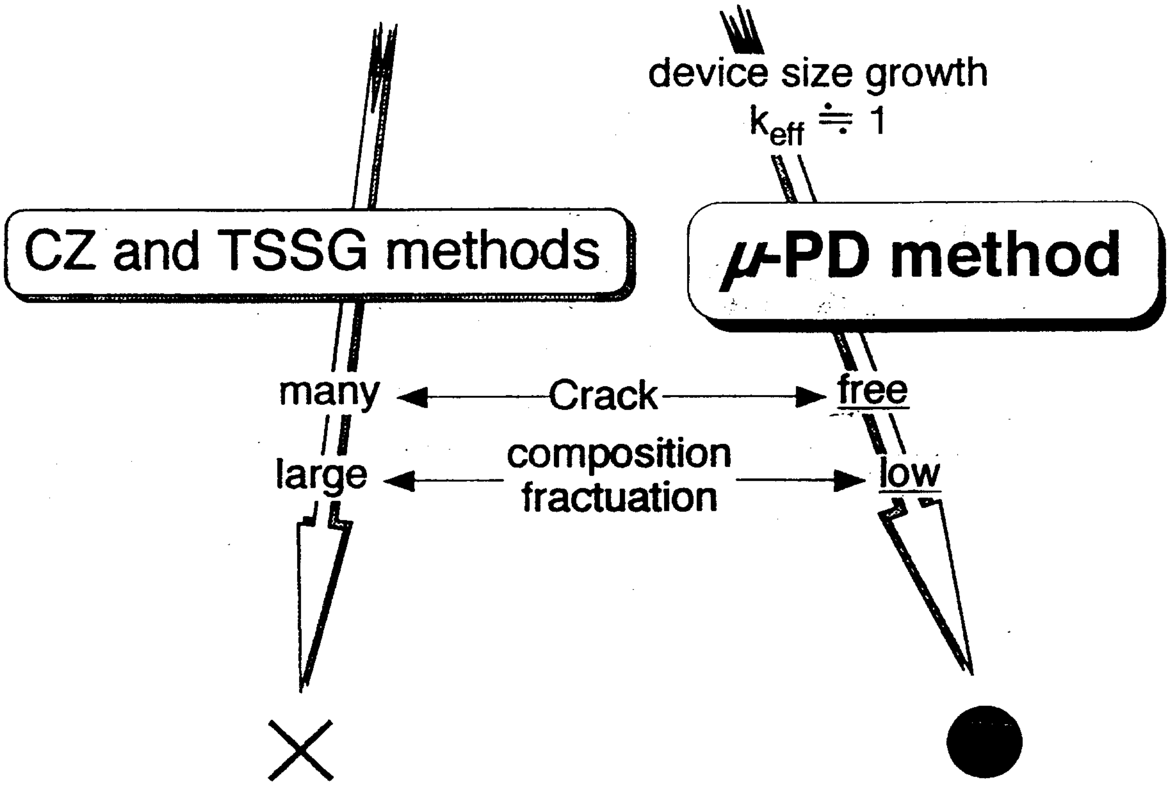


Blue SHG crystal

$KNbO_3$(KN): Small temperature allowance, Twin

$K_3Li_{2-X}Nb_{5+X}O_{15+2X}$(KLN):

- Large nonlinear coefficient
- No optical damage
- Mechanical and chemical stability



device size growth

$k_{eff} \doteqdot 1$

CZ and TSSG methods

μ-PD method

many ←Crack→ free

large ← composition fractuation → low

×

●

Micro single crystals

	dia. (μm)	orientation	pulling rate (mm/h)
Oxide			
$K_3Li_2Nb_5O_{15}$	150~1000	$\langle 100\rangle$, $\langle 001\rangle$	10~80
$K_3Li_2Ta_xNb_{5-x}O_{15}$	500~800	$\langle 100\rangle$	3~9
$LiNbO_3$	60~1200	$\langle 100\rangle$, $\langle 001\rangle$	12~90
$Ca_3(Nb,Ga)_{2-x}Ga_3O_{12}$	500~800	$\langle 111\rangle$	20
$KGd(WO_4)_2$	~500	$\langle 001\rangle$	6
$NaGd(WO_4)_2$	~500	$\langle 001\rangle$	20
$Ca_3Li_xNb_{1.5+x}Ga_{3.5-2x}O_{12}$	800~1200	$\langle 111\rangle$	3~18
$Pb_2NaZn_2V_3O_{12}$	800~1200	$\langle 111\rangle$	6
$NaCa_2Mg_2V_3O_{12}$	800~1200	$\langle 111\rangle$	6
$La_3Ga_5SiO_{14}$	500~800	$\langle 001\rangle$	20
Semiconductor			
Si	100~500	$\langle 111\rangle$	3~300
SiGe	500~1200	$\langle 111\rangle$	3~120

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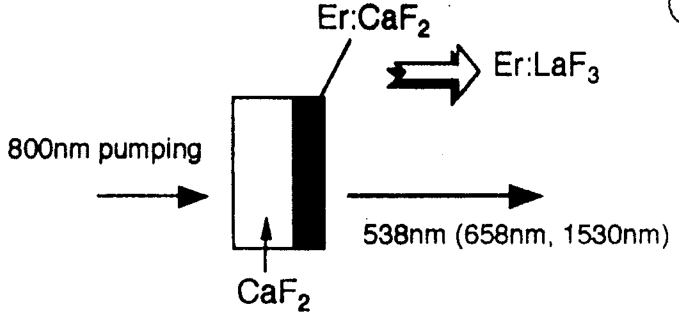
Device Structures for Efficient Up-conversion Laser

1st step: F



Er:CaF_2

Er:LaF_3

800nm pumping

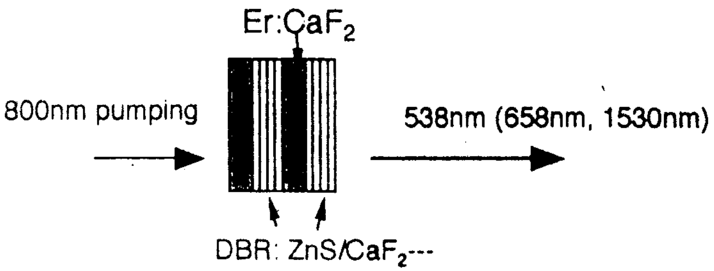
538nm (658nm, 1530nm)

CaF_2

Optimization of MBE growth
- Crystallinity
- Er doping: 1-20wt%

2nd step: Efficie sion

2-1. Micro-cavity enhancement



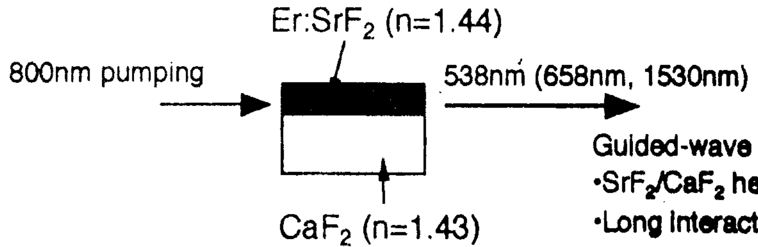
Er:CaF_2

800nm pumping

538nm (658nm, 1530nm)

DBR: ZnS/CaF_2---

2-2. Guided-wave confinement



Er:SrF_2 (n=1.44)

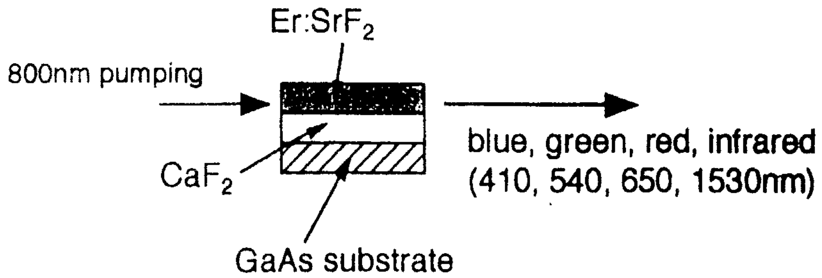
800nm pumping

538nm (658nm, 1530nm)

CaF_2 (n=1.43)

Guided-wave up-conversion
- SrF_2/CaF_2 heteroepitaxy
- Long interaction
- High density pumping

2-3. Guided-wave confinement Heteroepitaxy



Er:SrF_2

800nm pumping

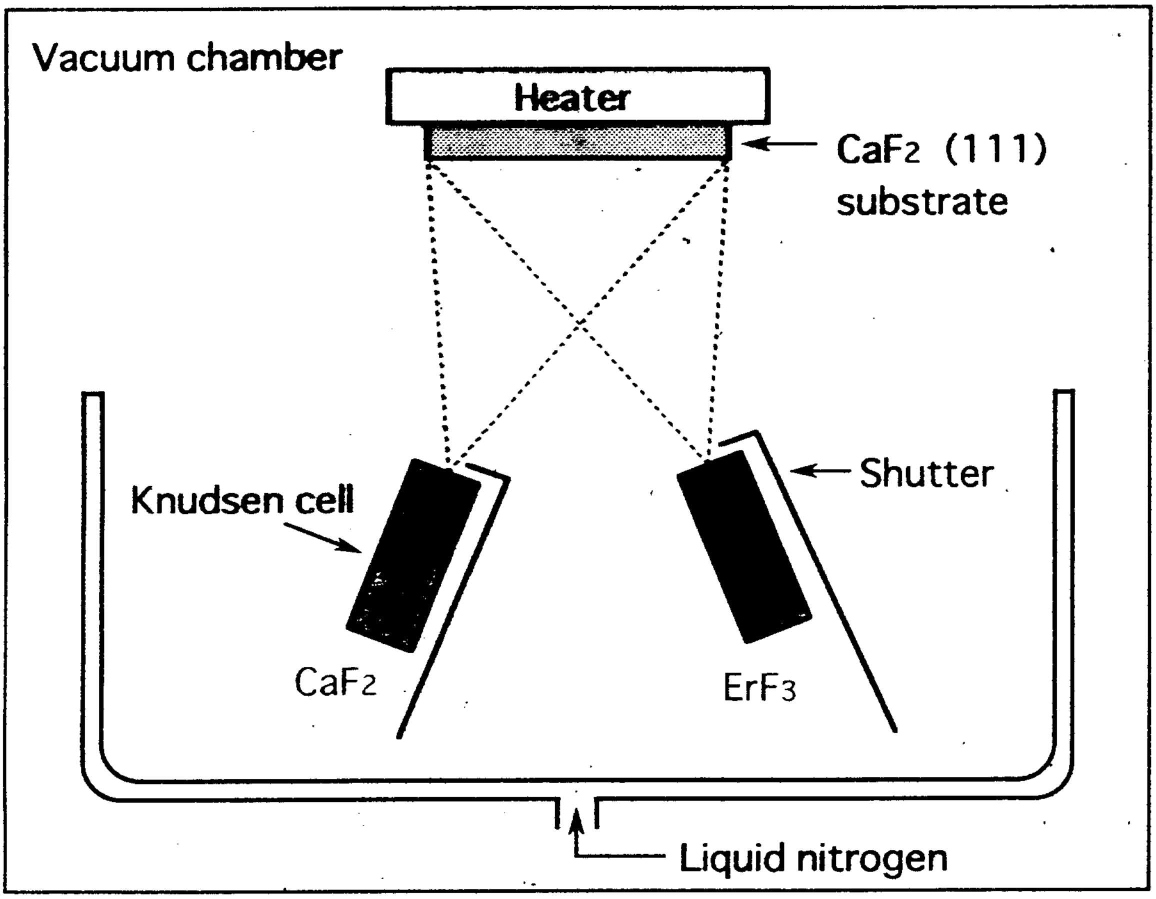
CaF_2

GaAs substrate

blue, green, red, infrared
(410, 540, 650, 1530nm)

- Experimental procedure

Schematic of MBE growth



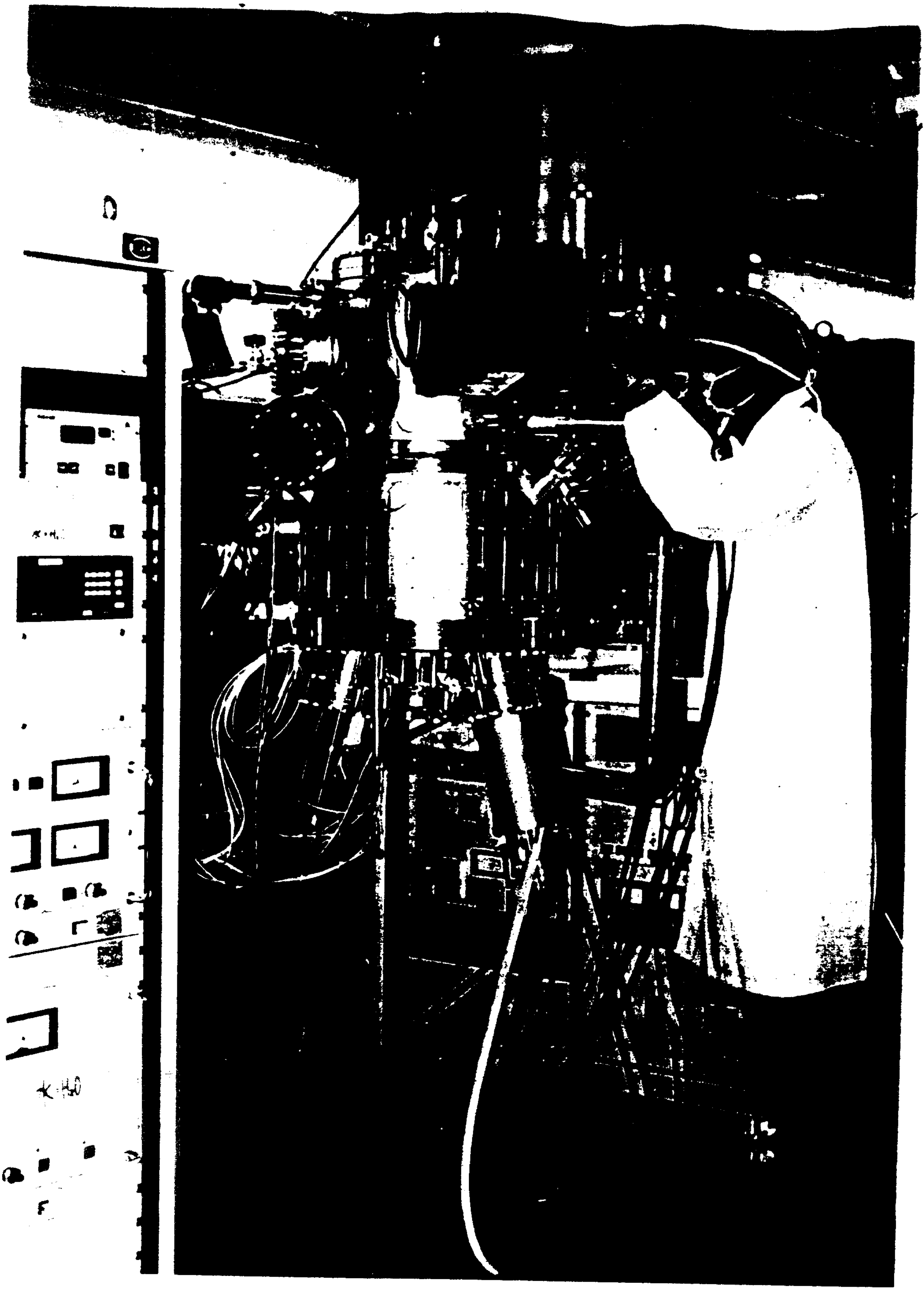
<Growth conditions>

Substrate temperature 450～550℃

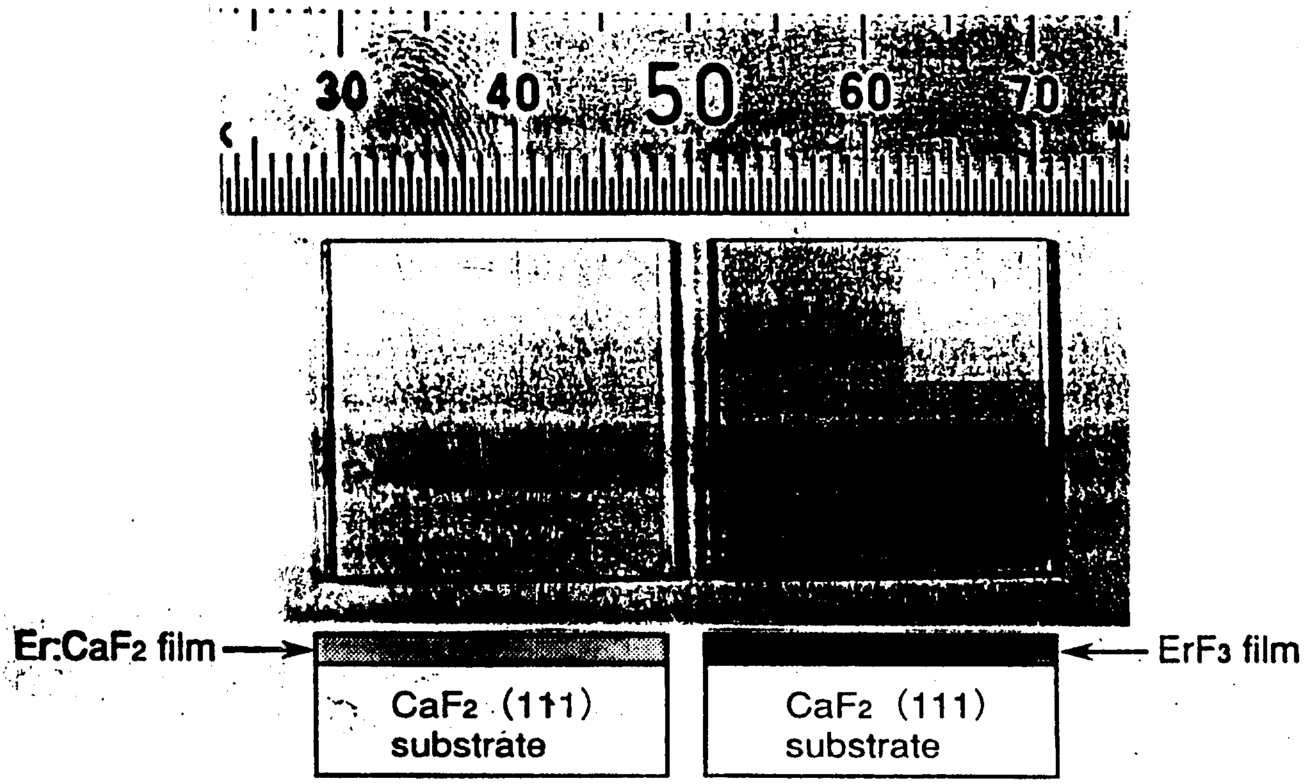
Growth rate 0.1～1.0μm/h

Film thickness around 1μm

Er^{3+} concentration 1.3～26wt%

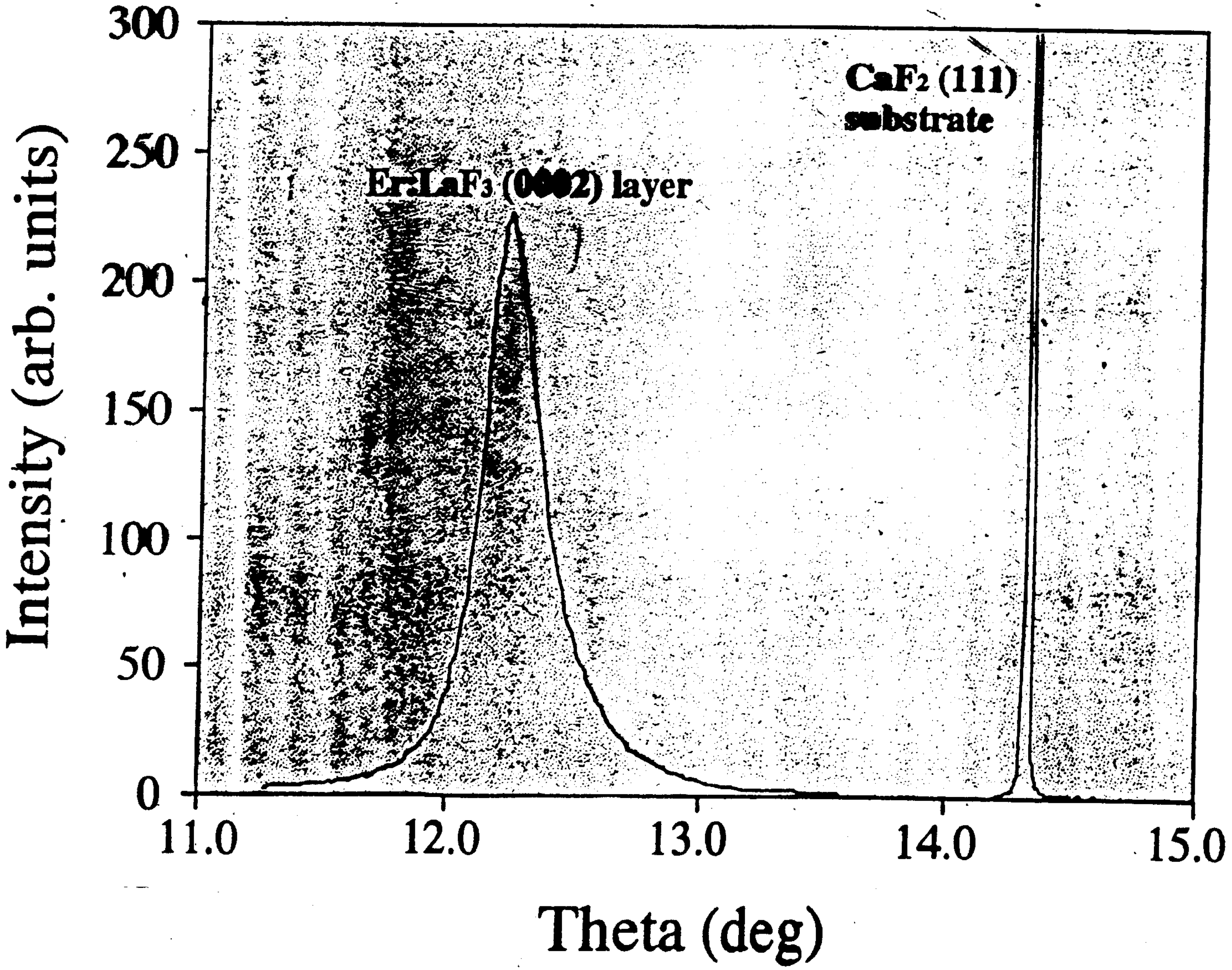


RHEED pattern of 1.36 wt% Er doped CaF_2 film
azimuth <1-2 1>

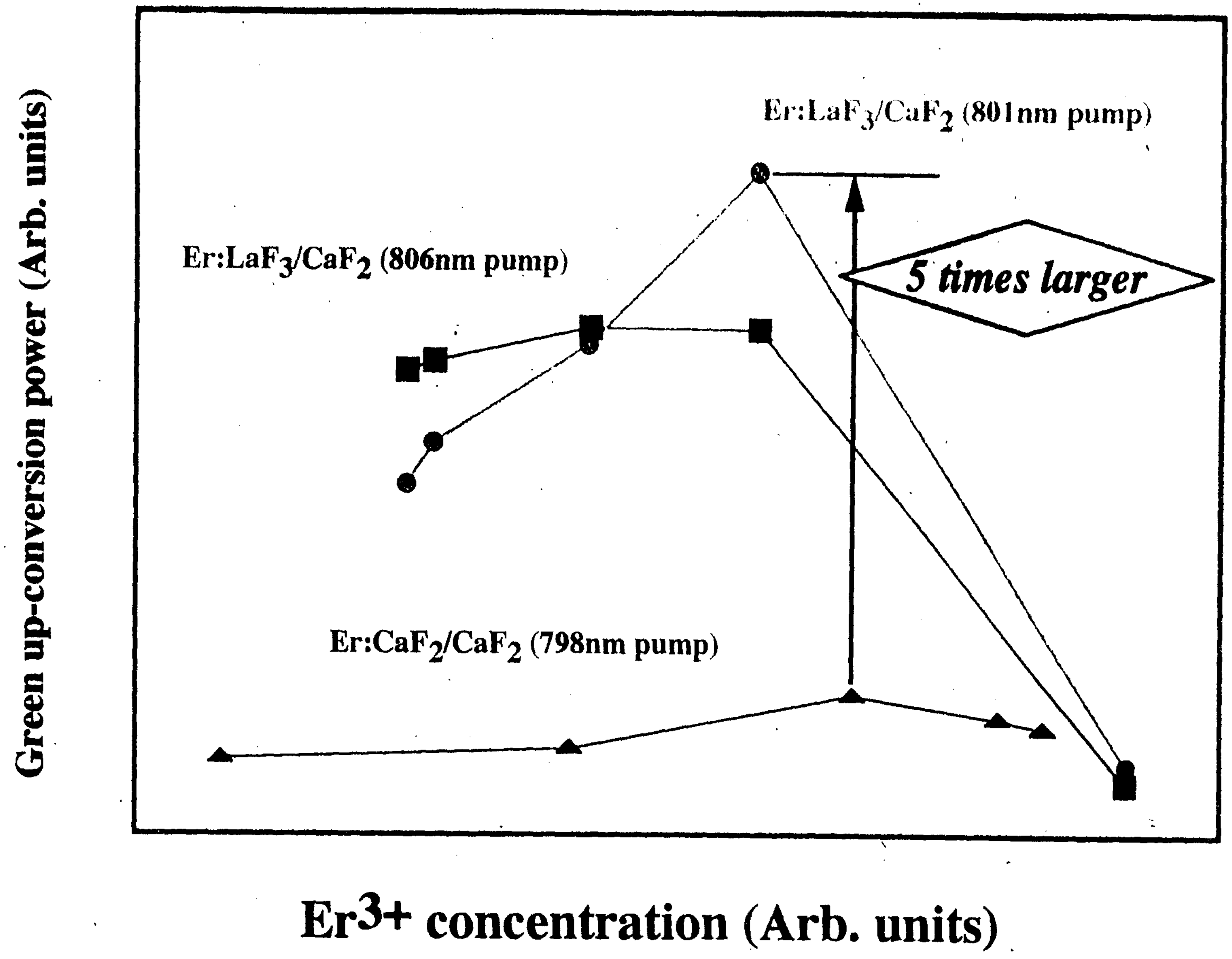


Er:CaF_2 and ErF_3 single crystal films grown by MBE technique

X-ray Rocking Curve Analysis



Dependence of up-conversion power on Er3+ concentration



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