MgO doping effect in $LiNbO_3$

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I. $LiNbO_3$

1. $LiNbO_3$ material

1) Piezo-electric, acousto-electric, opto-electric and non-linear optical properties.

2) Material for active optical wave-guide device fabrication.

3) Material for future optical usage (optical storage, etc.).

4) SHG(second harmonic generation) : frequency doubling.

2. Physical properties of $LiNbO_3$

1) Crystal structure

Trigonal, space group:R3c, point group:3m

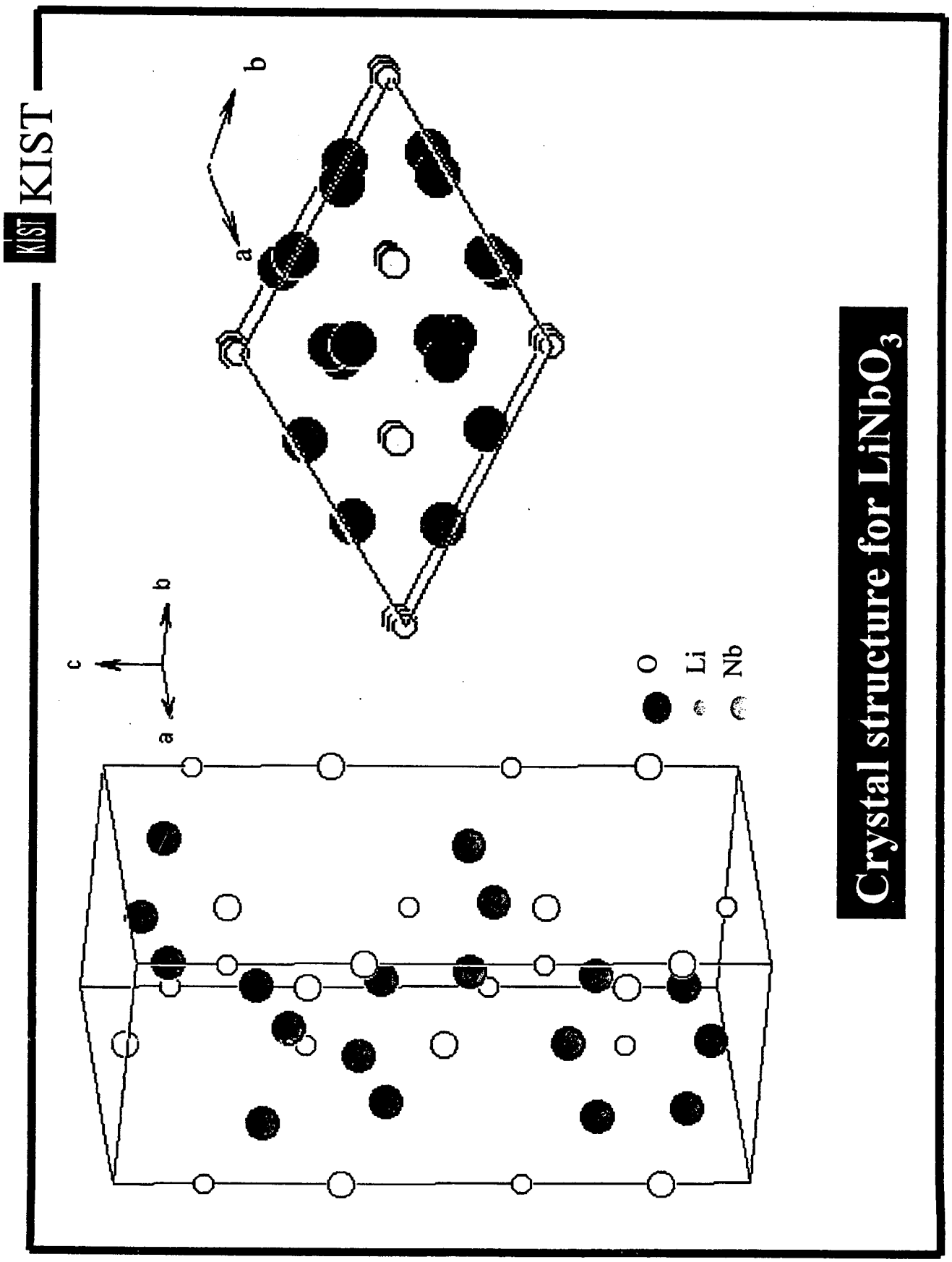
⇒ can be transformed to Hexagonal structure.

2) Phase diagram

⇒$LiNbO_3$ phase : congruent composition(melt growth).

3) Compositional variation : property variation.

4) MgO addition : ameliorate some properties of LN.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Crystal structure for $LiNbO_3$
b
a
c
b
a
O
Li
Nb

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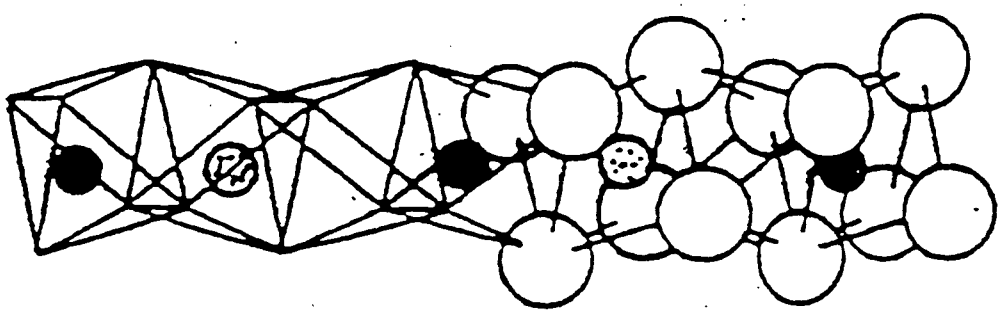

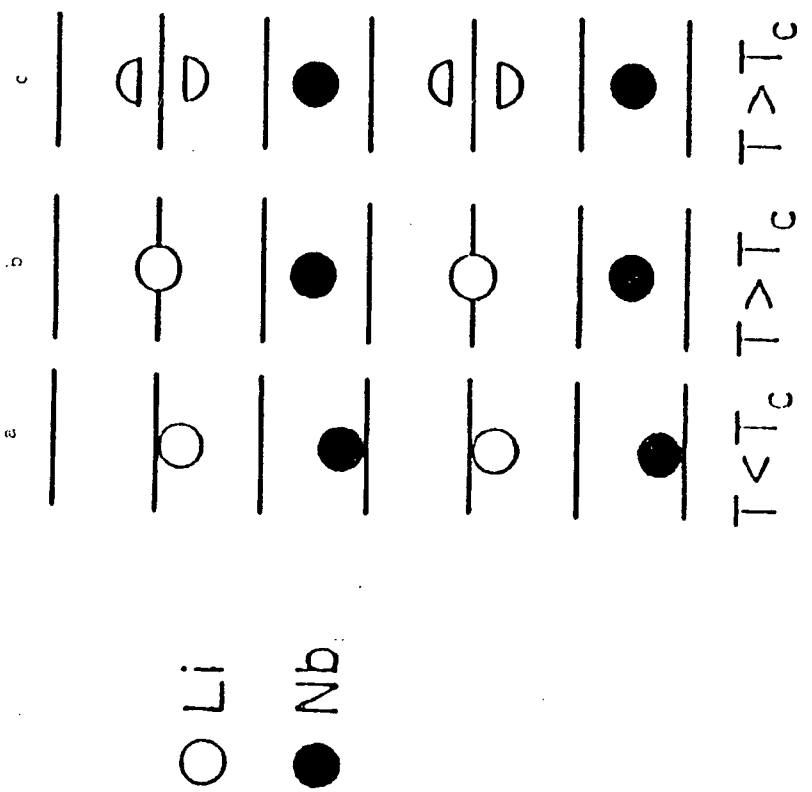

Crystal structure for $LiNbO_3$

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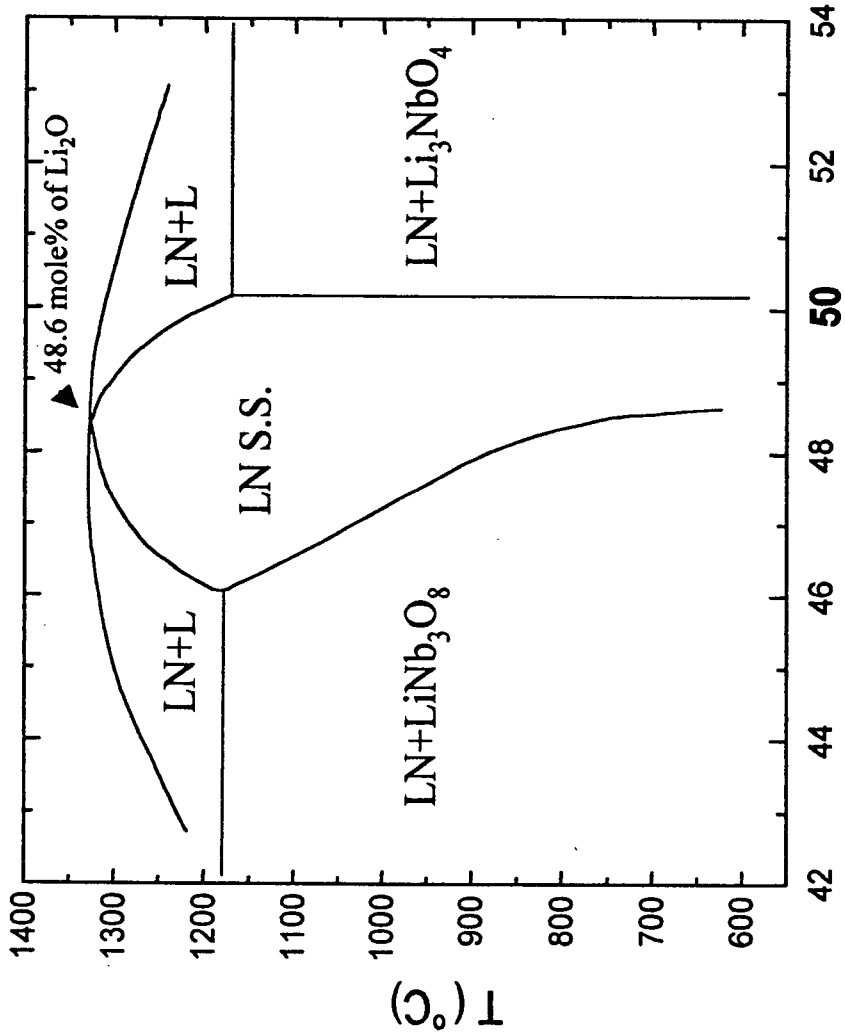

Phase diagram for $LiNbO_3$

Properties of $LiNbO_3$ sensitive to the Li/Nb ratio

Dependence	Measured quantity
Strong	Curie temperature
	Birefringence
	Phase-matching SHG temp.
	NMR line broadening
	Diffusion coefficient
Weak	Lattice parameters, Density
	Dielectric constant
	Refractive index
	Electro-optic coefficient
	Nonlinear optic coefficient

3. $LiNbO_3$ application

1) SAW(surface acoustic wave) filter

: cellular phone

2) Optical modulator, deflector, switch, memory for optical communication

3) Infrared detector, temperature sensor, pyrovision

II. Single crystal growth for $LiNbO_3$

1. $LiNbO_3$ single crystals growth methods

1) Czochralski method

2) Bridgman method

3) Floating zone method

4) Flux method

5) Kyropulous method

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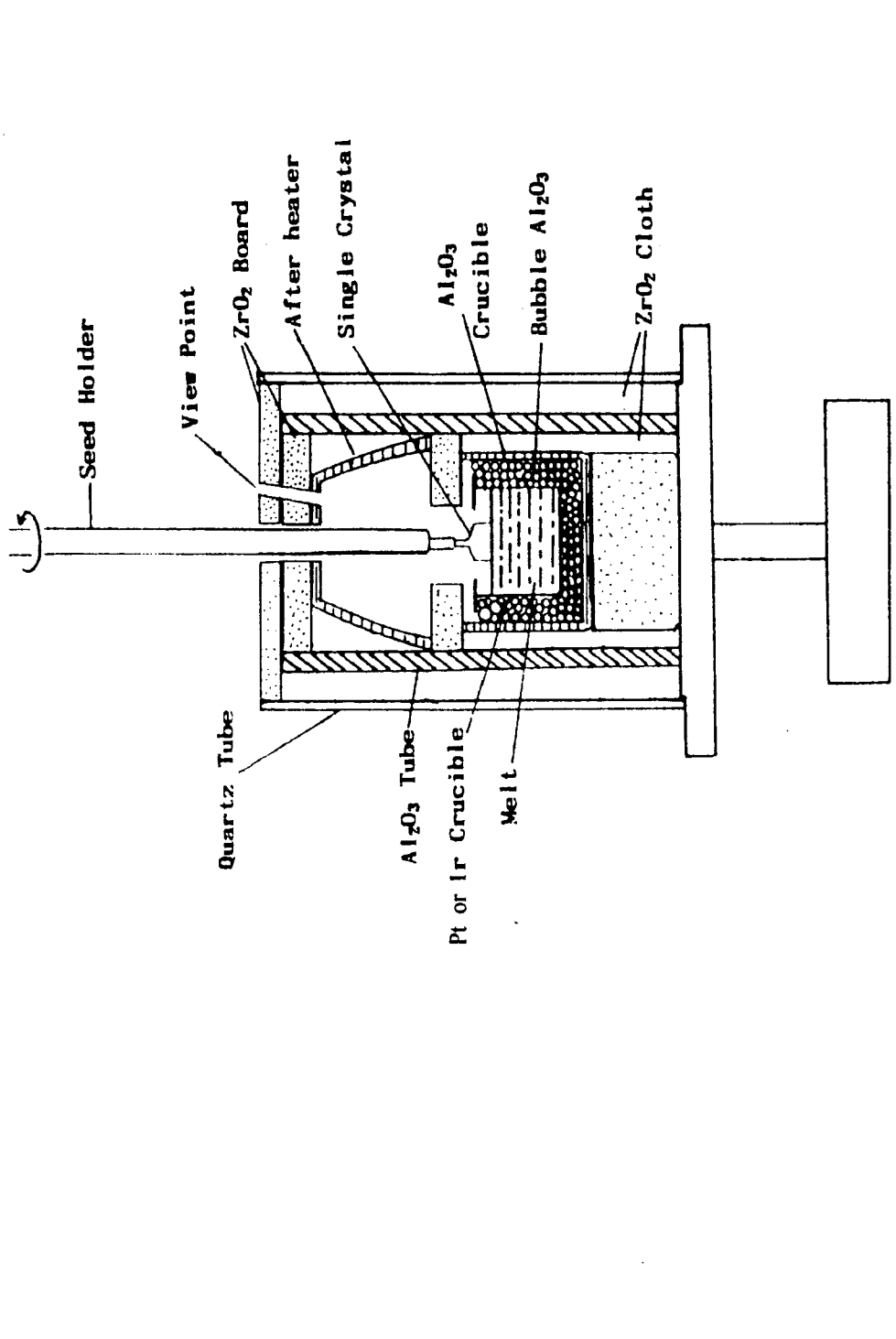


Schematic diagram of Czochralski method

2. $LiNbO_3$ samples preparation

Mixing & calcination

▼

Charging & melting

▼

Dipping & necking

▼

Shouldering & body growing

▼

Tailing & cooling

▼

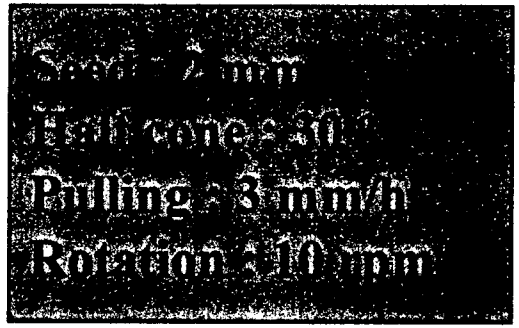
Annealing

▼

Wafering

▼

Poling



1200 °C - 10 hrs

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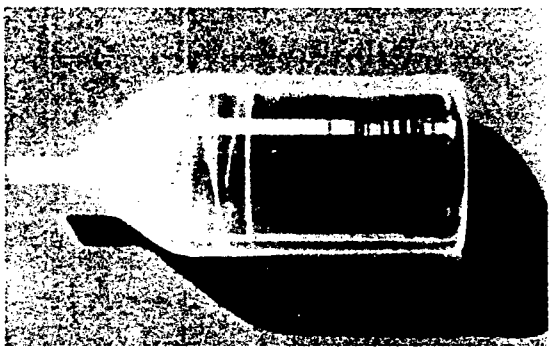
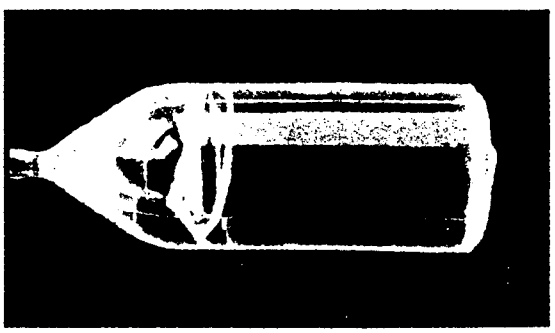
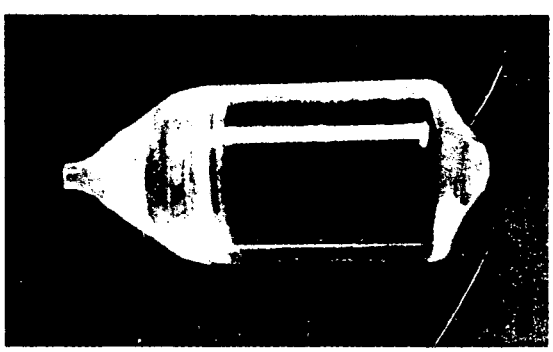


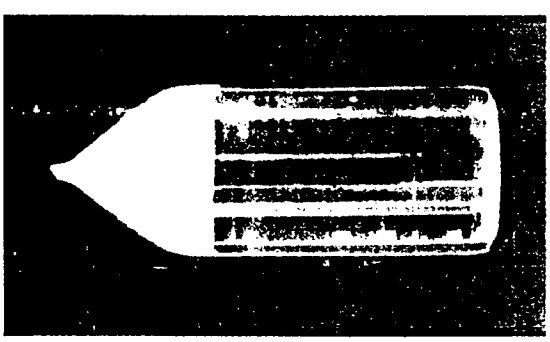
d) 4MgO:LN



c) 3MgO:LN



b) 2MgO:LN



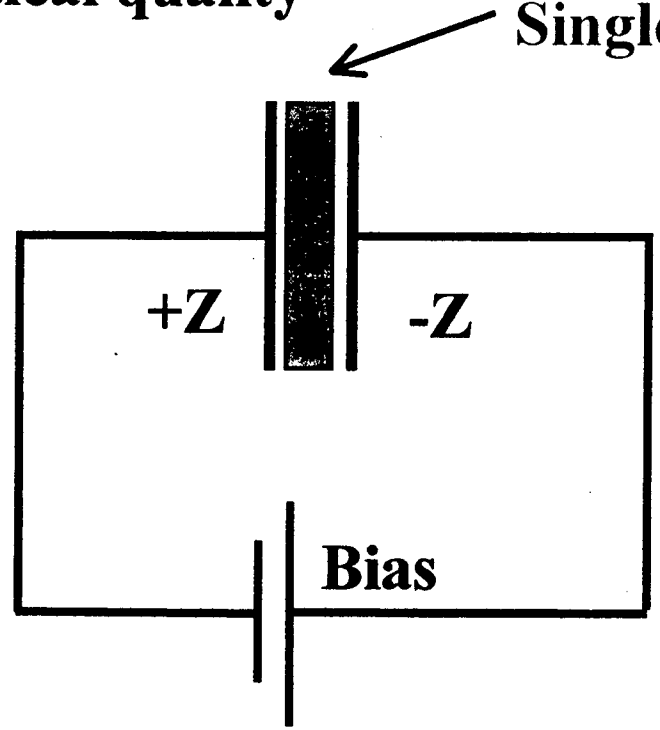
a) 1MgO:LN

Single crystals grown by Czochralski method

3. Poling

1) To make single domain
2) To improve optical quality

1200°C,10min
5V/cm



Schematic diagram of poling instrument

III. Optical properties of $LiNbO_3$

1. MgO doping in $LiNbO_3$

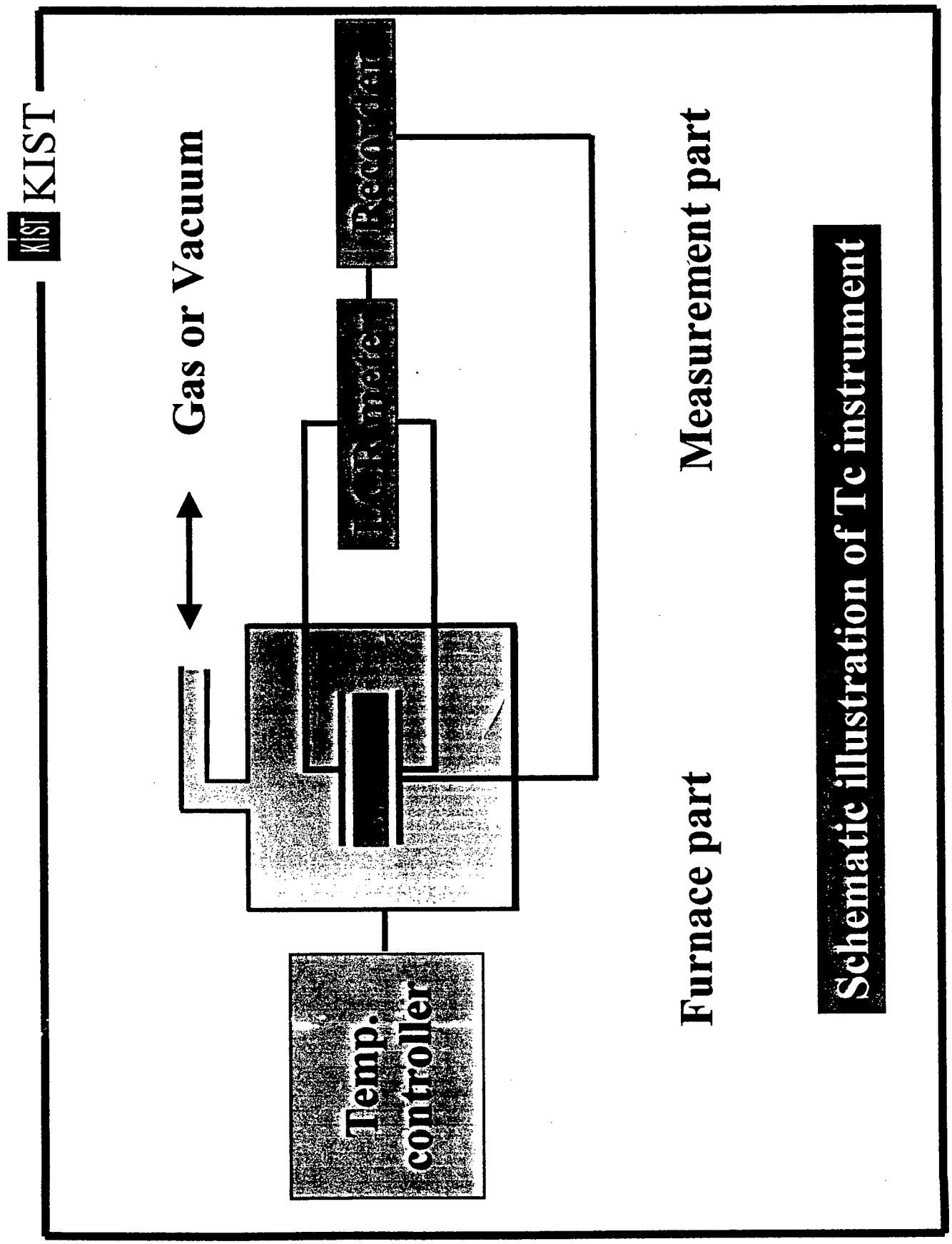
1) Crack prevention

2) Resistance increase against optical damage

3) Curie temperature is increased

4) SHG temperature can be modulated

5) Compensation for refractive increase caused by Li out-diffusion


KIST
Gas or Vacuum
Temp. controller
Furnace part
Measurement part
Schematic illustration of Tc instrument

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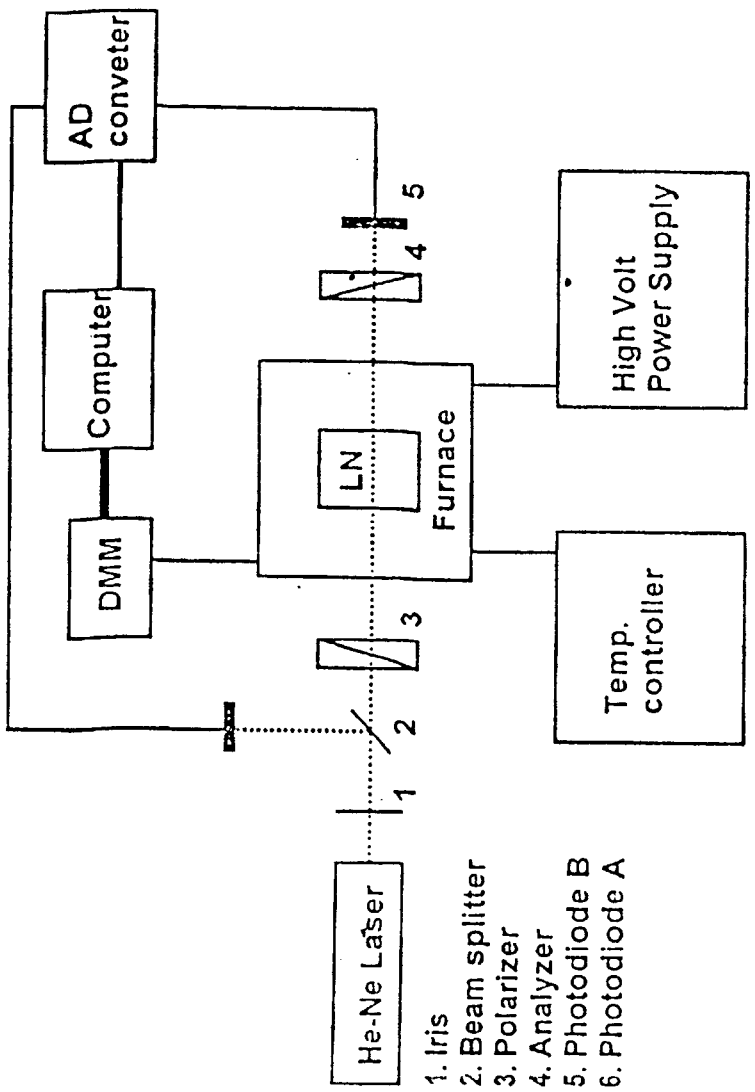

Schematic illustration of SHG instrument

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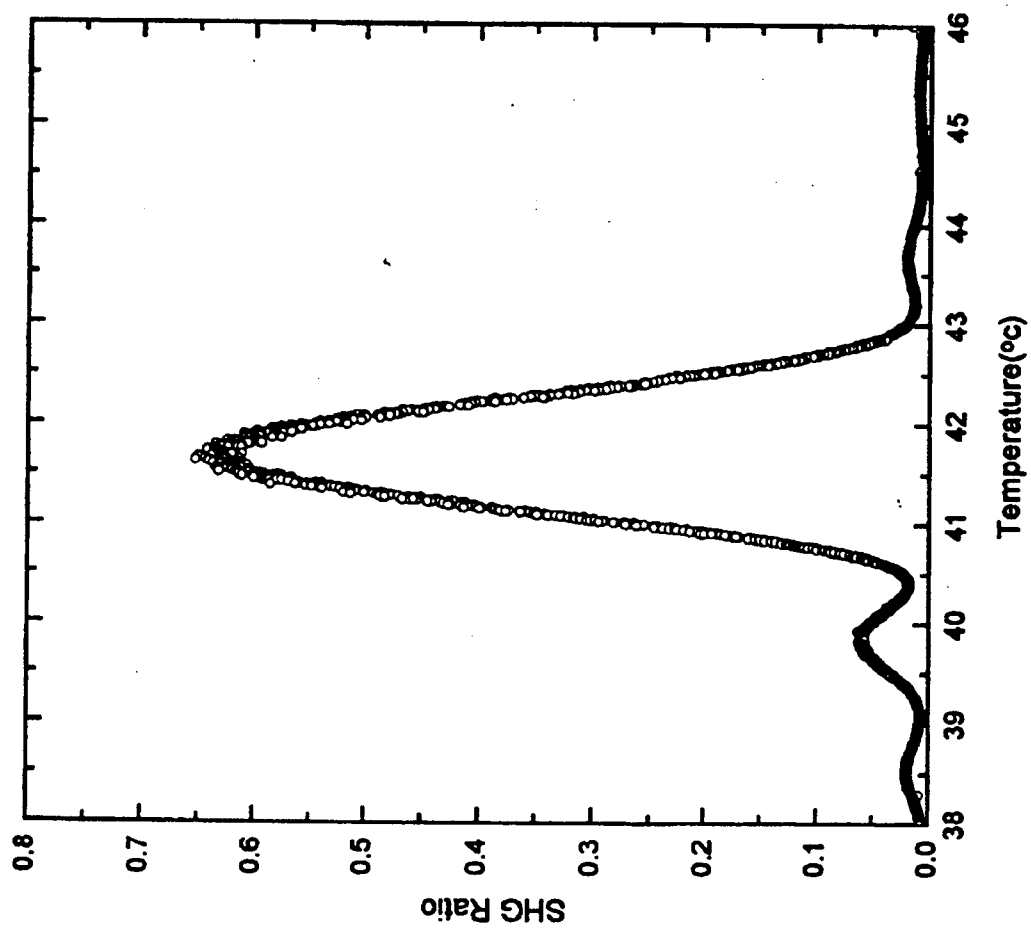
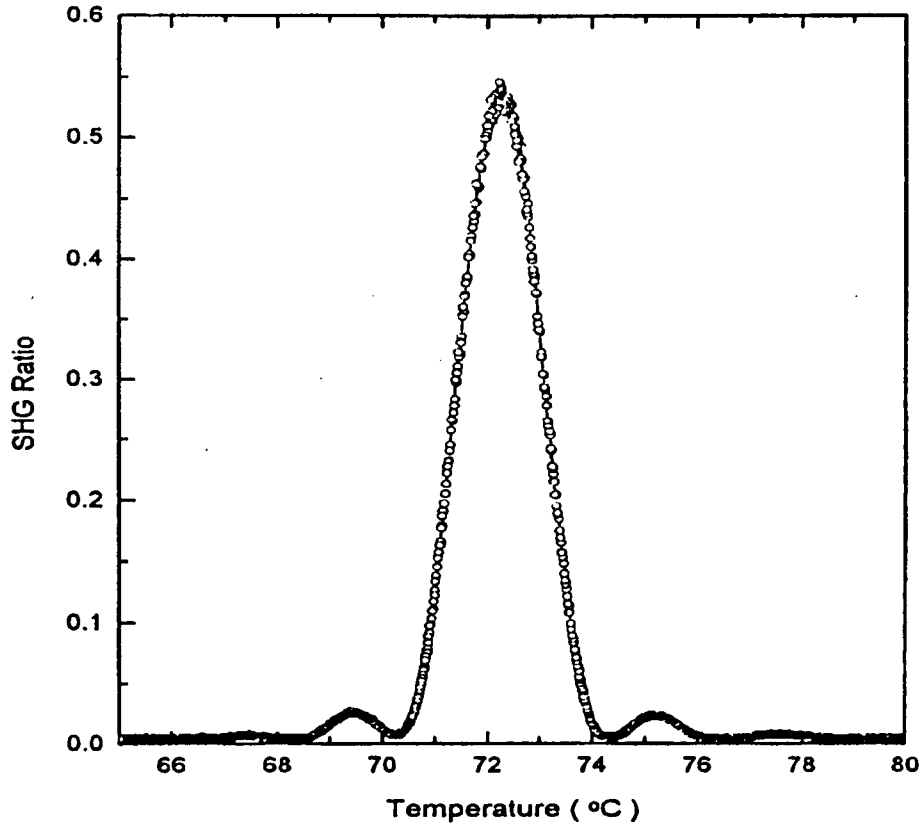


Phase matching temperature profile of 1 mole% MgO-doped $LiNbO_3$

$MgO:LiNbO_3$ single crystals : good quality confirmed by SHG



Phase matching temperature profile of 2 mole% MgO-doped $LiNbO_3$

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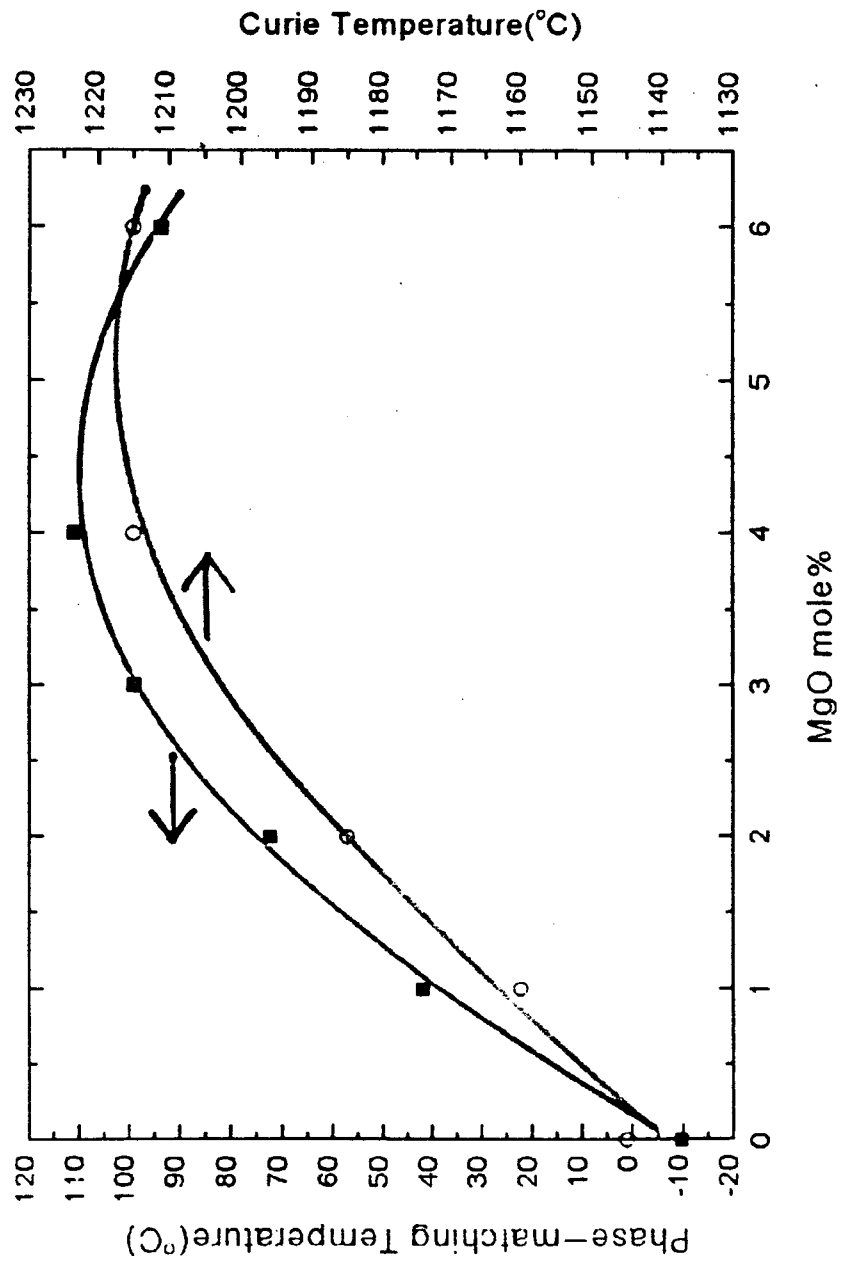
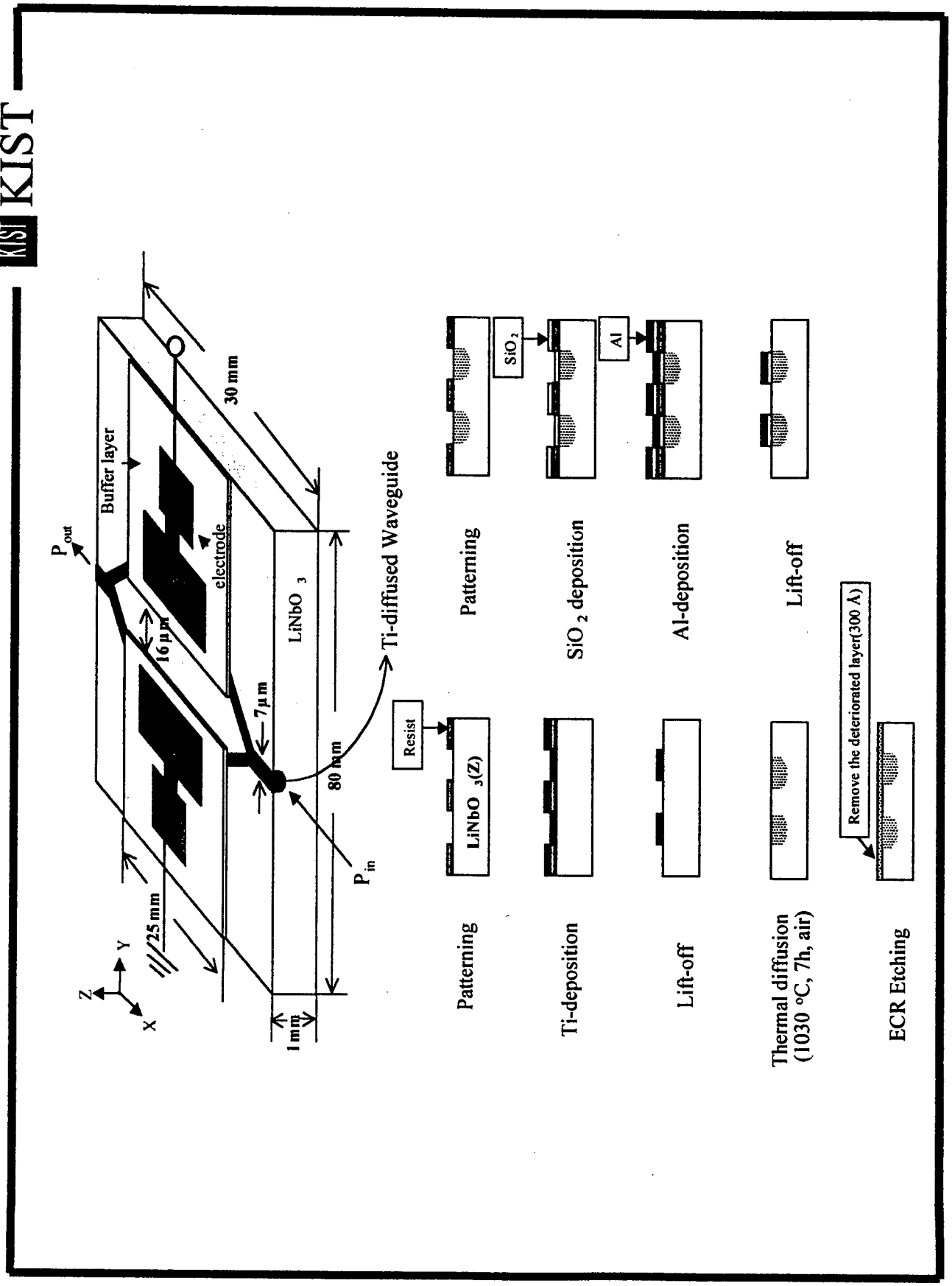


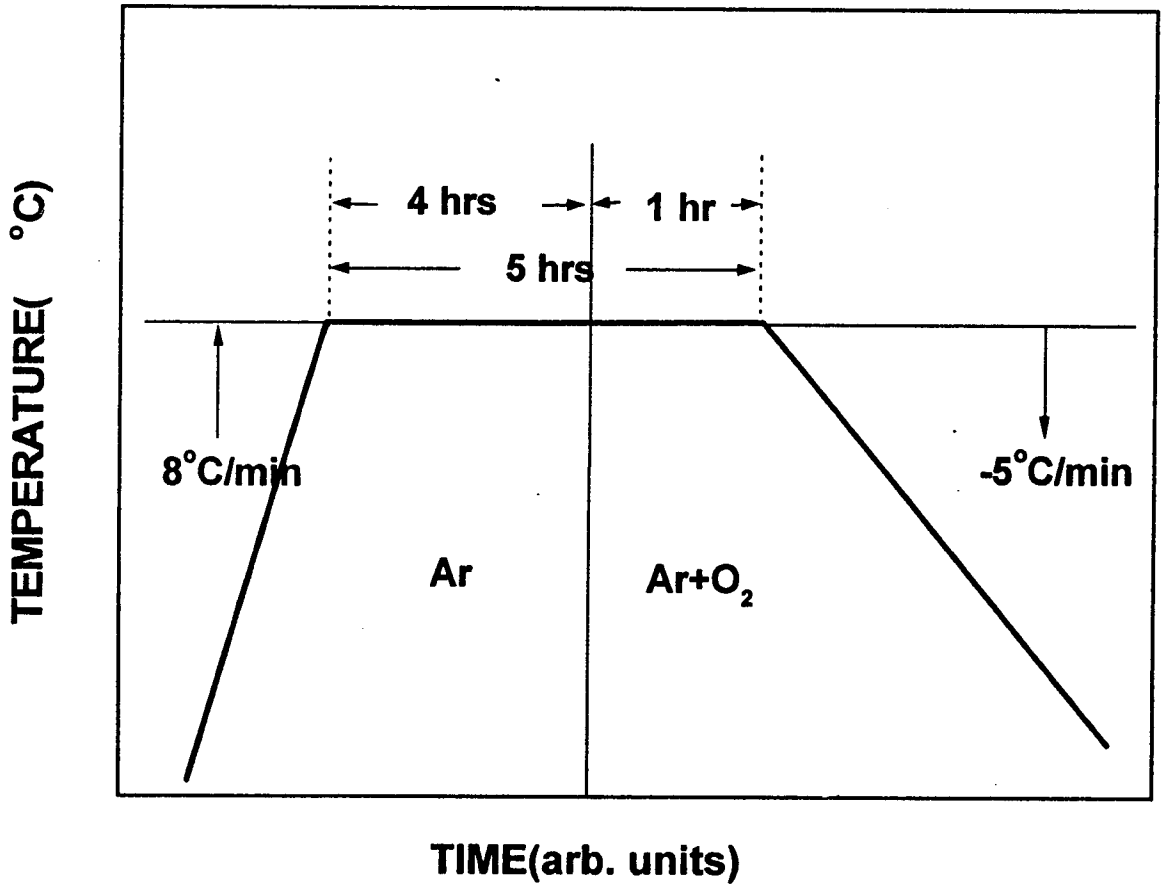
Phase matching temp. & Curie temp. of MgO:$LiNbO_3$

IV. Waveguide fabrication in $LiNbO_3$

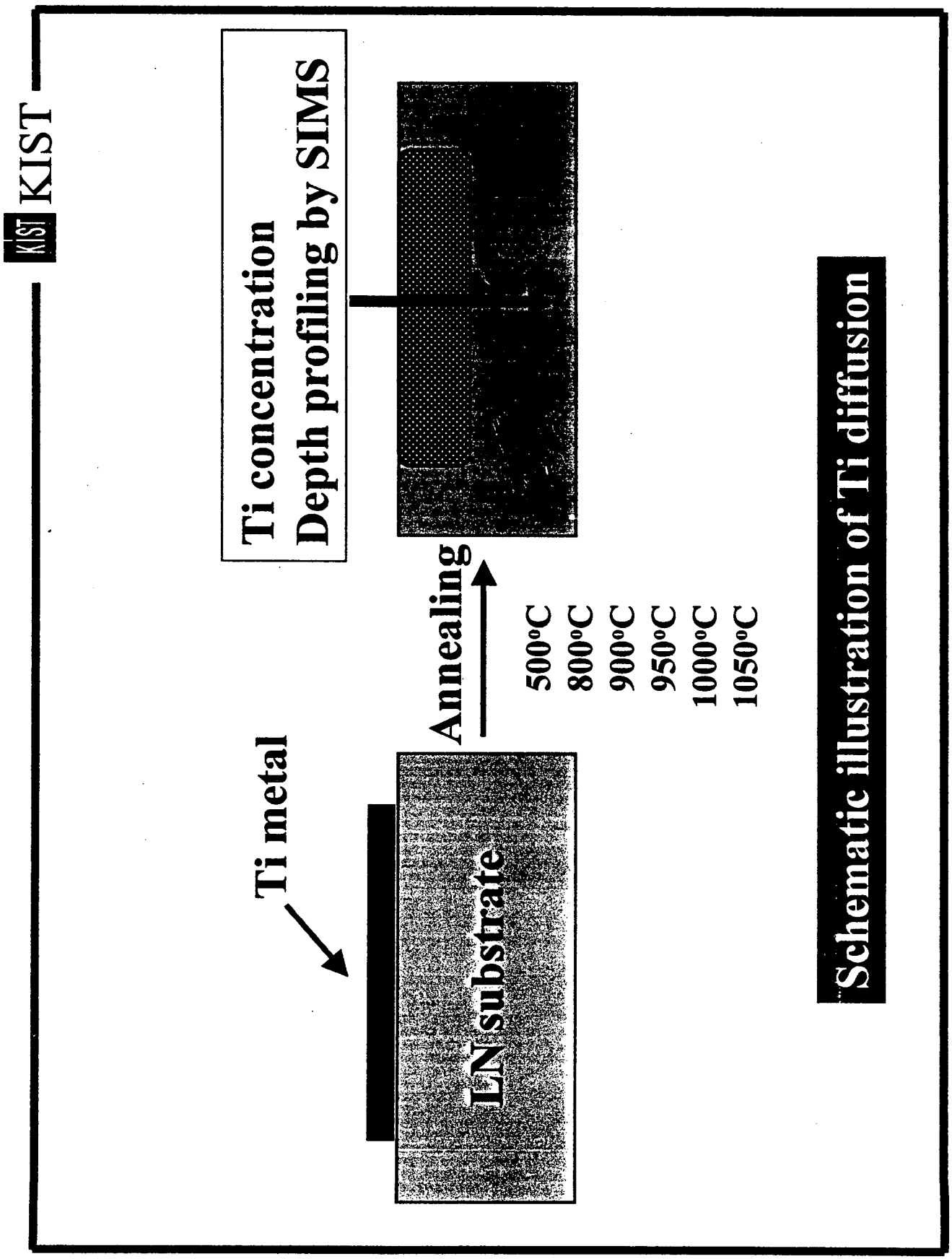
1. $LiNbO_3$ crystal substrates
   - Congruent composition $LiNbO_3$
   - MgO : 0.65, 1, 2, 3 mole%
   - Size : 10 × 10 × 2 mm
   - poling : 1200 °C, 5 V/cm, 10 min
   - -Z axis

2. Ti diffusion
   - Ti metal evaporation, 500 Å thickness
   - Thermal treatments (500, 800, 900, 950, 1000, 1050 °C)
   - SIMS analysis (CAMECA IMS 4f)

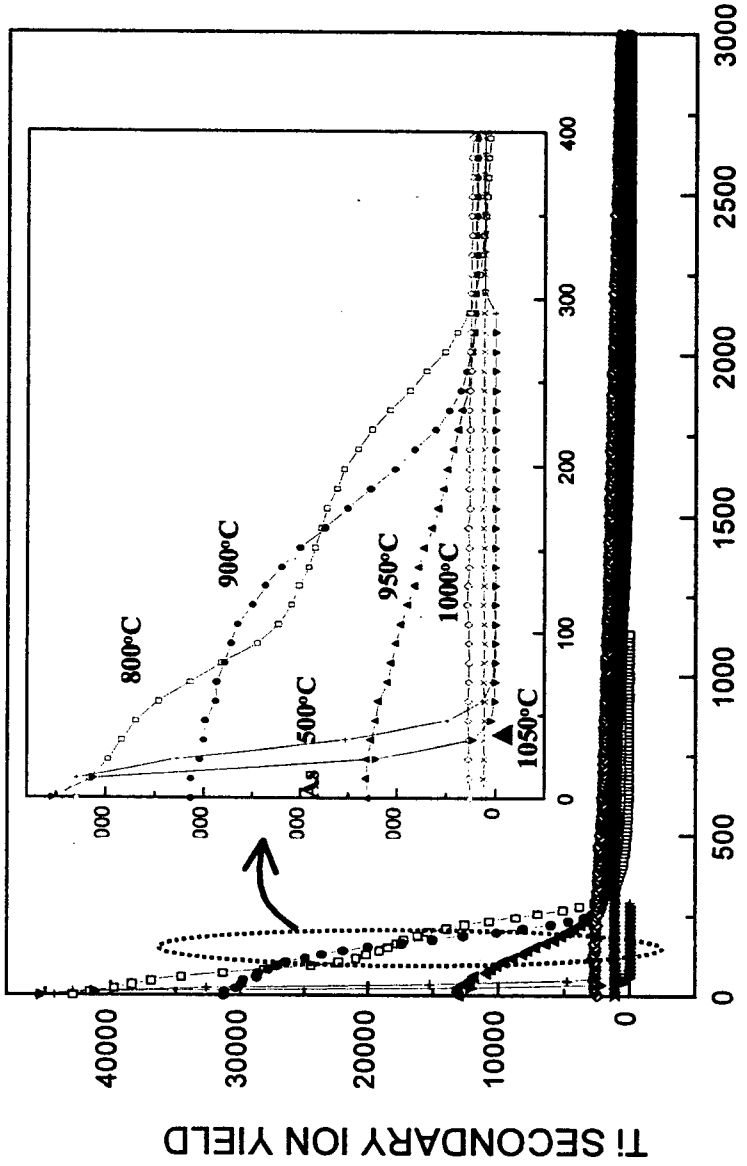

KIST
P_{out}
Buffer layer
electrode
16 μm
7 μm
30 mm
$LiNbO_3$
Ti-diffused Waveguide
80 mm
P_{in}
25 mm
1 mm
Y
Z
X
Resist
$LiNbO_3$(Z)
Patterning
Ti-deposition
Lift-off
Thermal diffusion
(1030 °C, 7h, air)
ECR Etching
Remove the deteriorated layer(300 Å)
Patterning
SiO_2
SiO_2 deposition
Al
Al-deposition
Lift-off



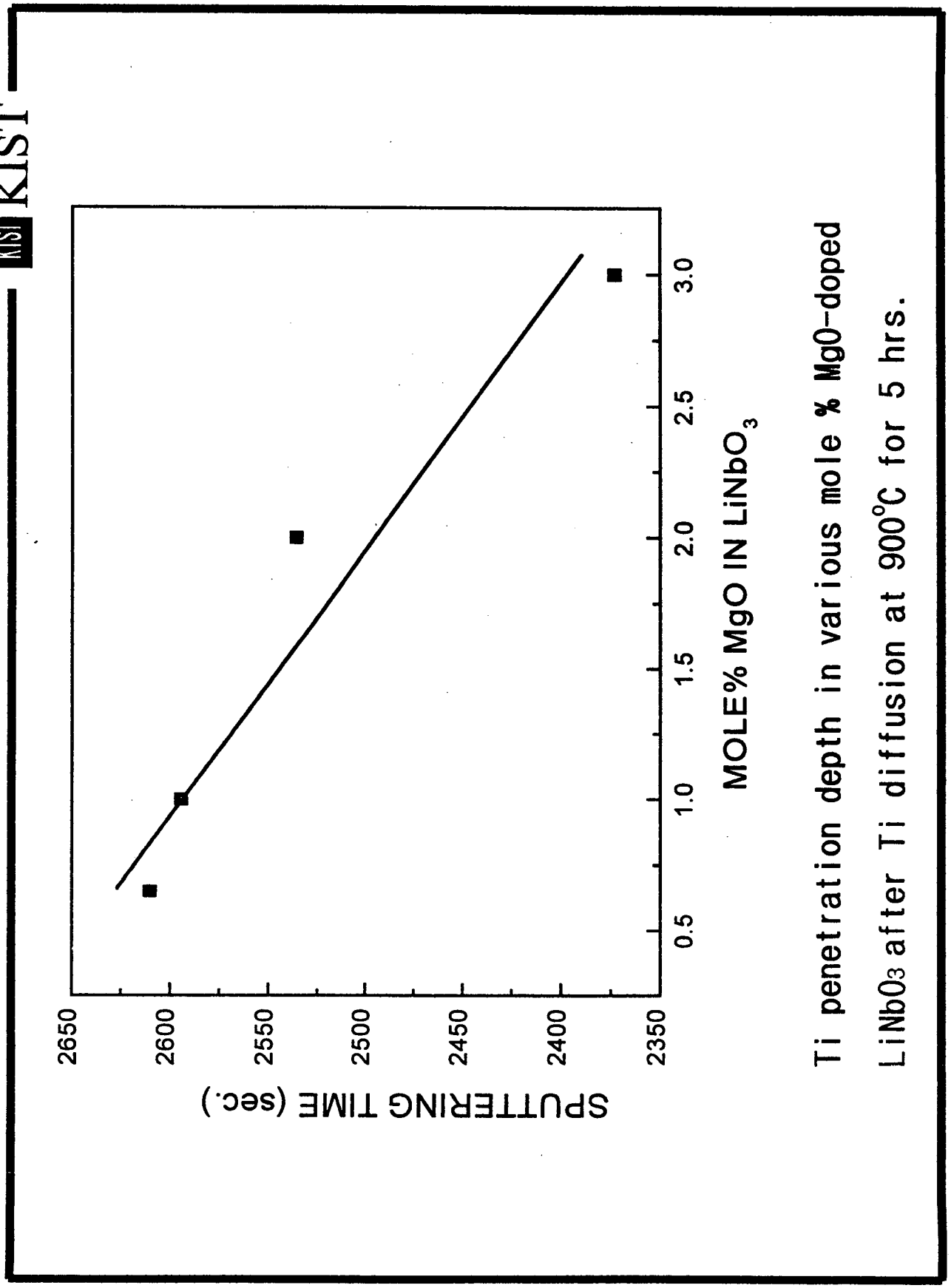
Heating process of Ti diffusion into MgO-doped $LiNbO_3$. The 5 hrs of annealing temperatures are 500, 800, 900, 950, 1000, and 1050 °C, respectively.

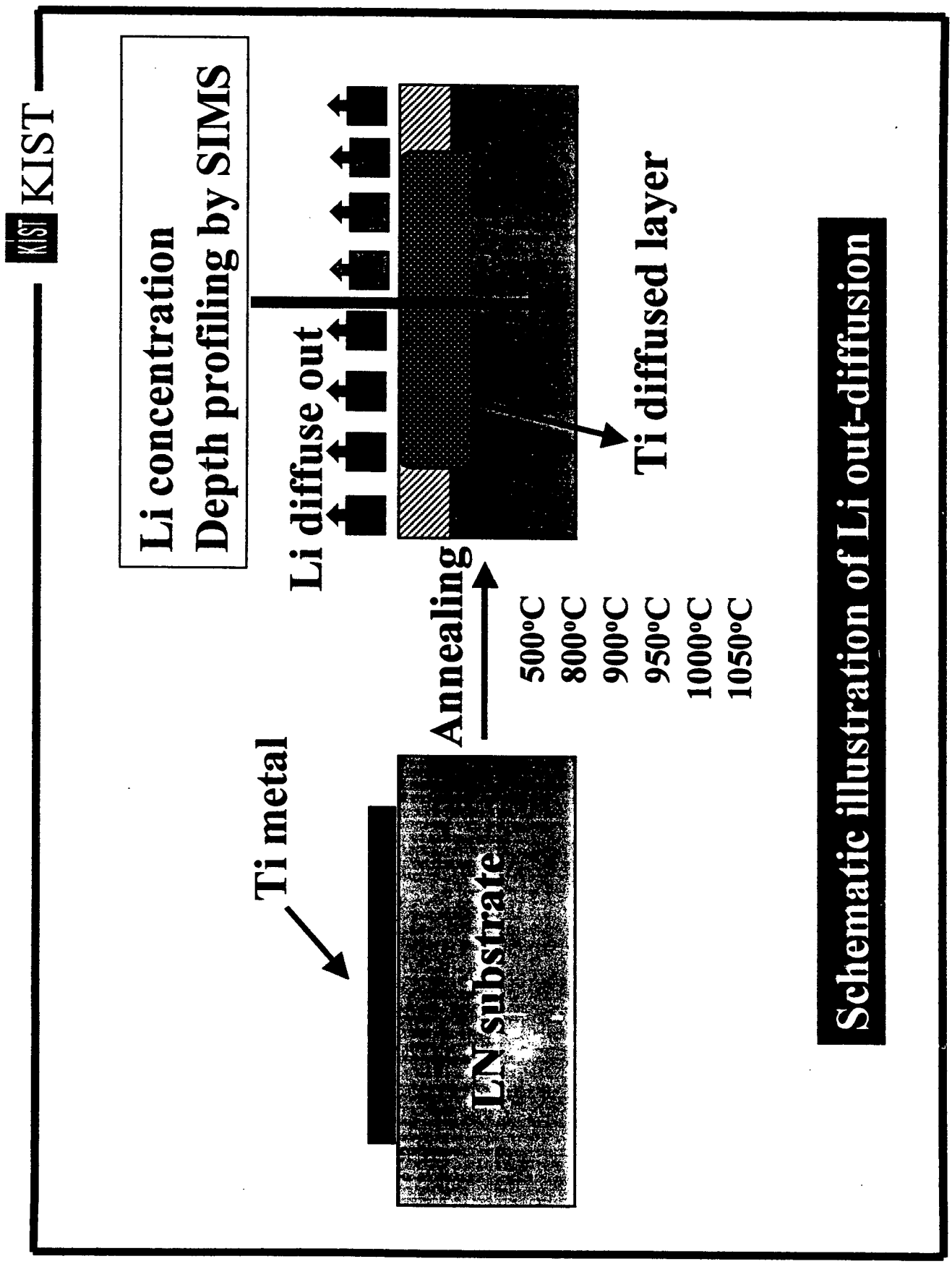

KIST
Ti concentration
Depth profiling by SIMS
Ti metal
LN substrate
Annealing
500°C
800°C
900°C
950°C
1000°C
1050°C
Schematic illustration of Ti diffusion

KIST

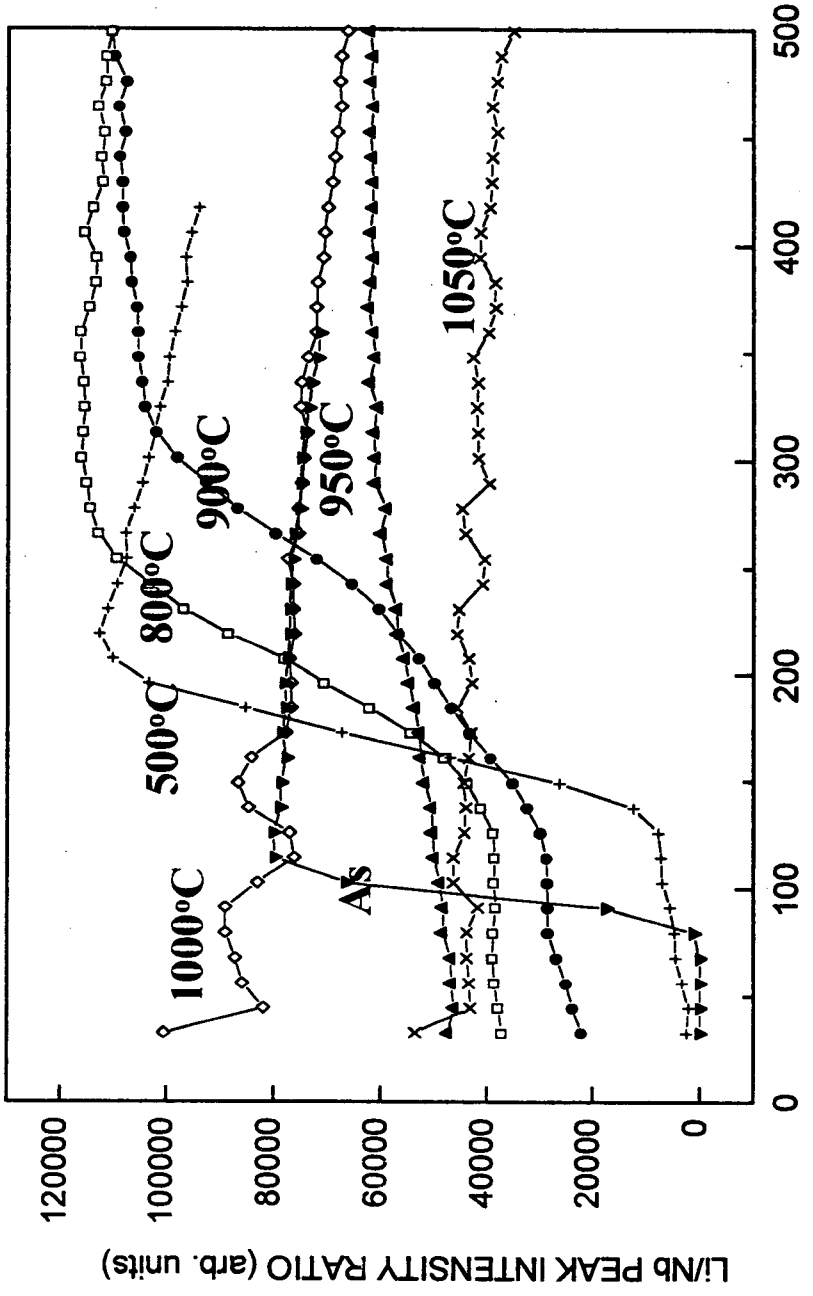


SIMS depth profiles of Ti in 0.65 mole% MgO-doped $LiNbO_3$ at various temperatures for 5 hrs.

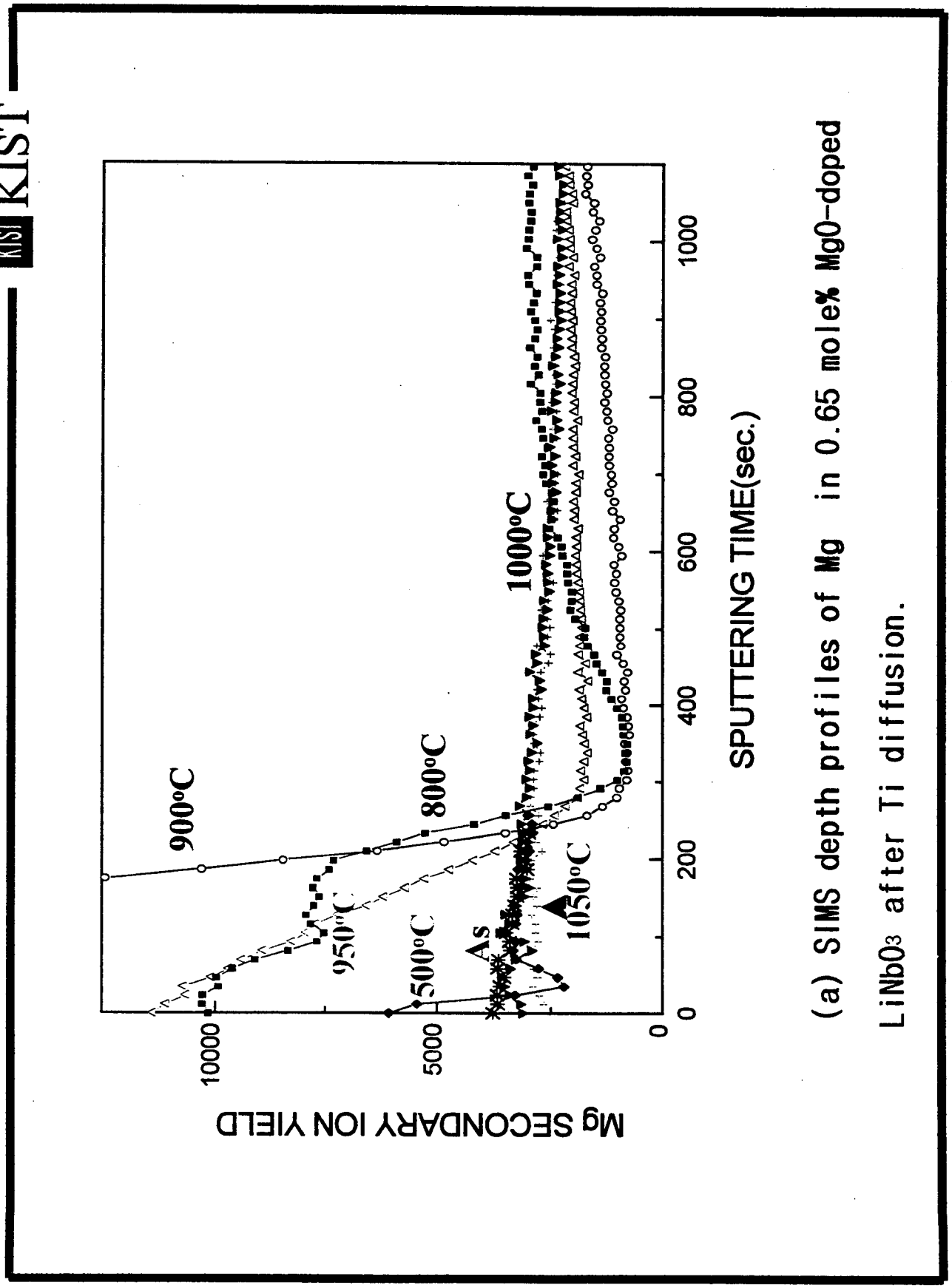

KIST
Ti penetration depth in various mole % MgO-doped
LiNbO3 after Ti diffusion at 900°C for 5 hrs.
SPUTTERING TIME (sec.)
2650
2600
2550
2500
2450
2400
2350
0.5
1.0
1.5
2.0
2.5
3.0
MOLE% MgO IN LiNbO3

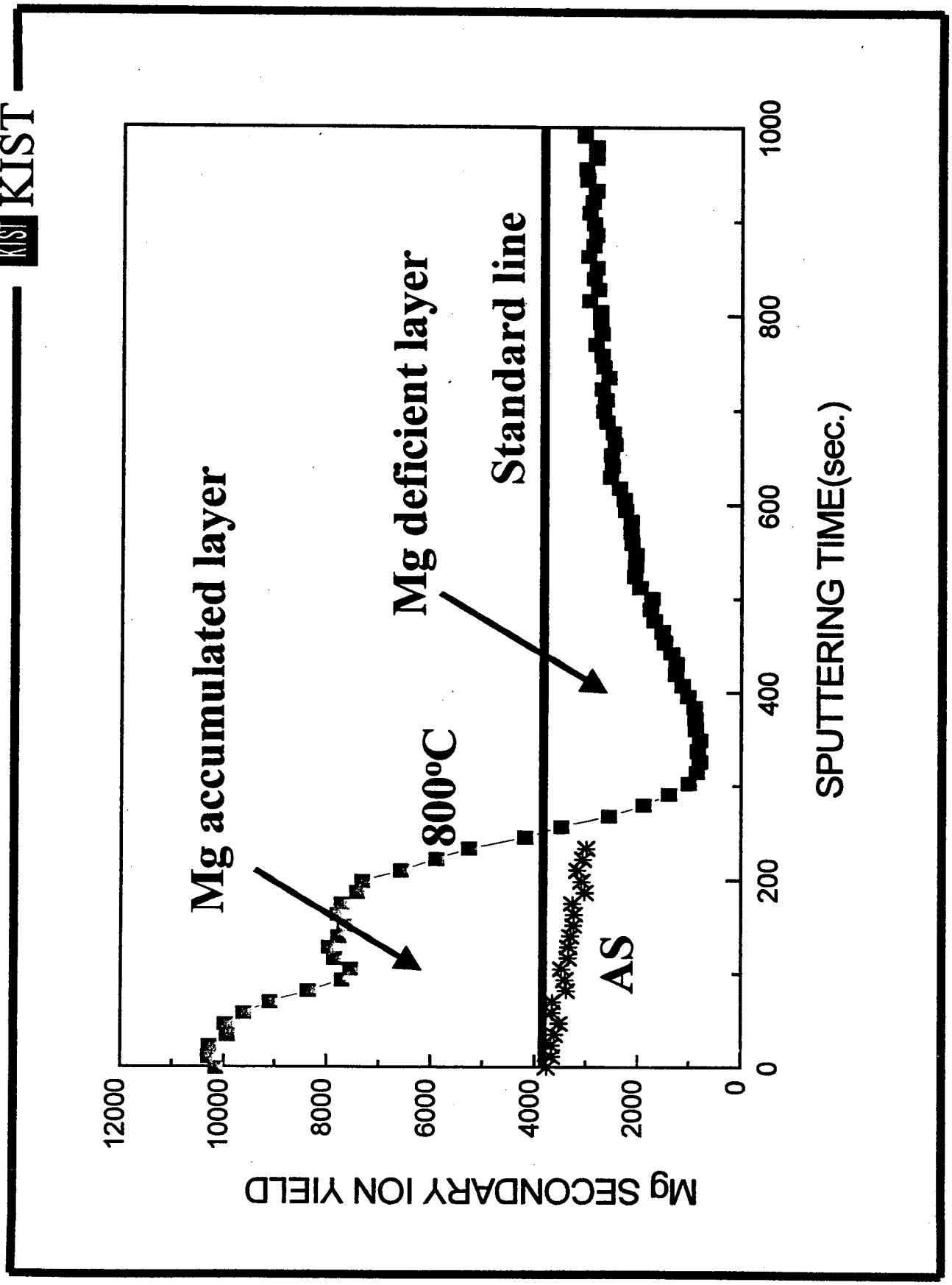

KIST
Li concentration
Depth profiling by SIMS
Li diffuse out
Ti diffused layer
Annealing
500°C
800°C
900°C
950°C
1000°C
1050°C
Ti metal
LN substrate
Schematic illustration of Li out-diffusion

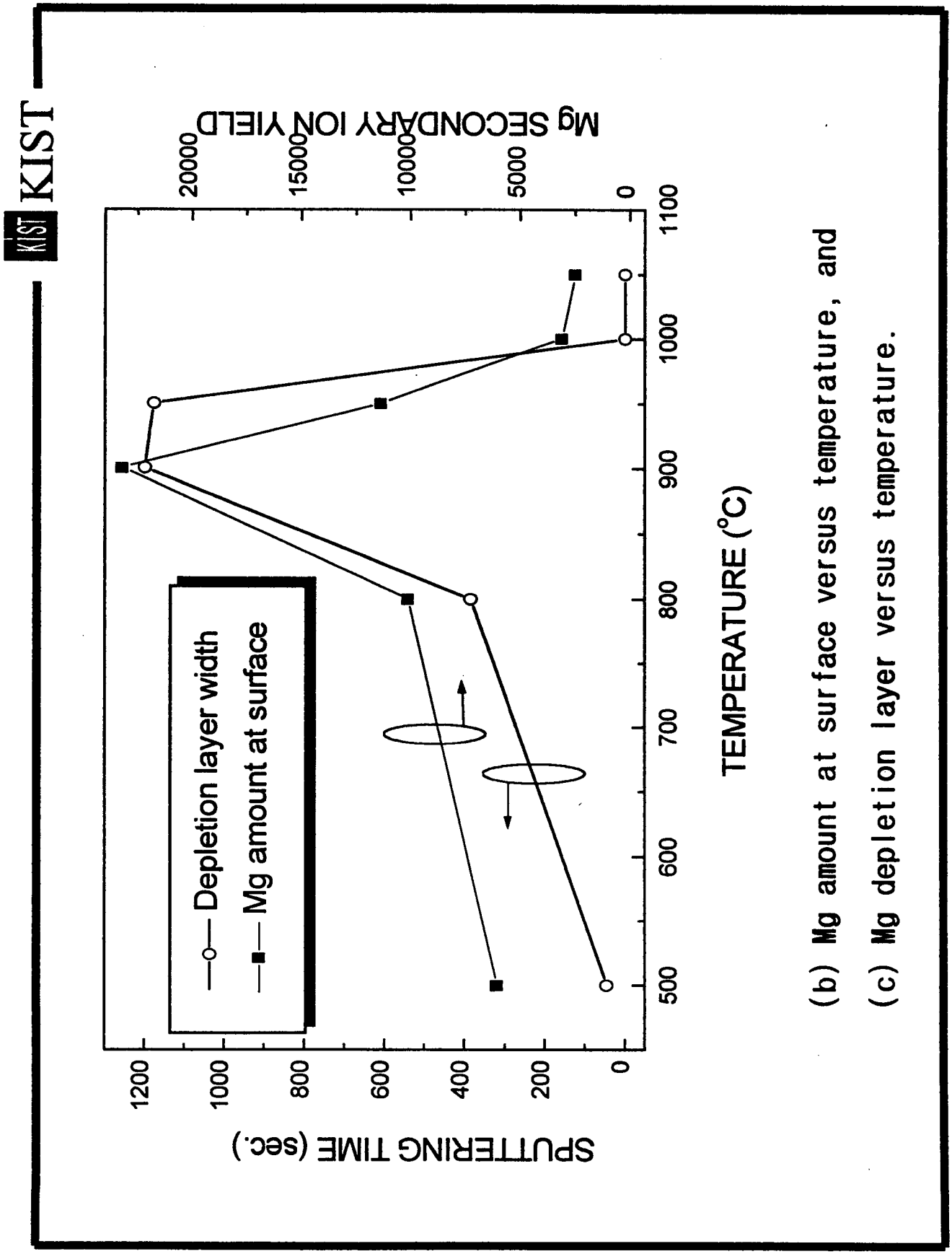
KIST KIST



SIMS depth profiles of Li in 0.65 mole % MgO-doped $LiNbO_3$ after Ti diffusion at various temperatures for 5 hrs.

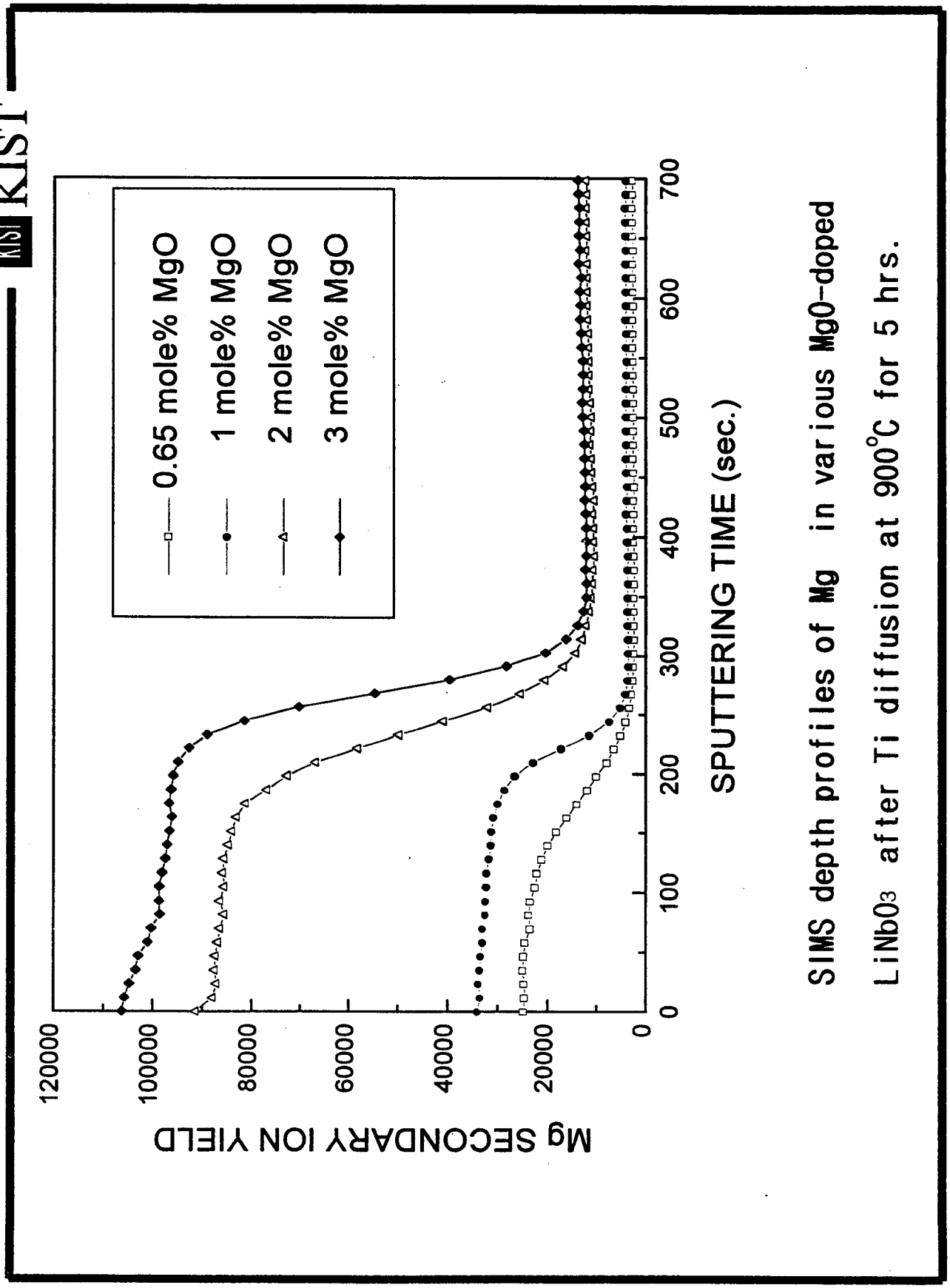

KIST
Mg SECONDARY ION YIELD
10000
5000
0
0
200
400
600
800
1000
SPUTTERING TIME(sec.)
900°C
800°C
1000°C
950°C
500°C
As
1050°C
(a) SIMS depth profiles of Mg in 0.65 mole% MgO-doped
LiNbO3 after Ti diffusion.


KIST
Mg accumulated layer
Mg deficient layer
Standard line
800°C
AS
Mg SECONDARY ION YIELD
SPUTTERING TIME(sec.)
12000
10000
8000
6000
4000
2000
0
0
200
400
600
800
1000



(b) Mg amount at surface versus temperature, and

(c) Mg depletion layer versus temperature.


KIST
0.65 mole% MgO
1 mole% MgO
2 mole% MgO
3 mole% MgO
Mg SECONDARY ION YIELD
SPUTTERING TIME (sec.)
120000
100000
80000
60000
40000
20000
0
0
100
200
300
400
500
600
700
SIMS depth profiles of Mg in various MgO-doped
LiNbO3 after Ti diffusion at 900°C for 5 hrs.

- Diffusion equation

1) Ti in-diffusion : limited source diffusion (Gaussian equation)

$$C_x = \frac{\alpha}{2\sqrt{\pi Dt}} \exp\left(-\frac{x^2}{4Dt}\right)$$

2) Li out-diffusion : constant source diffusion (error function)

$$C_x = C_{Li}' erf\left(\frac{x}{2\sqrt{Dt}}\right)$$

- Defect model

1) Stoichiometric $LiNbO_3$

$[Li][Nb]O_3$

2) Congruent $LiNbO_3$(Li/Nb = 48.6/51.4)

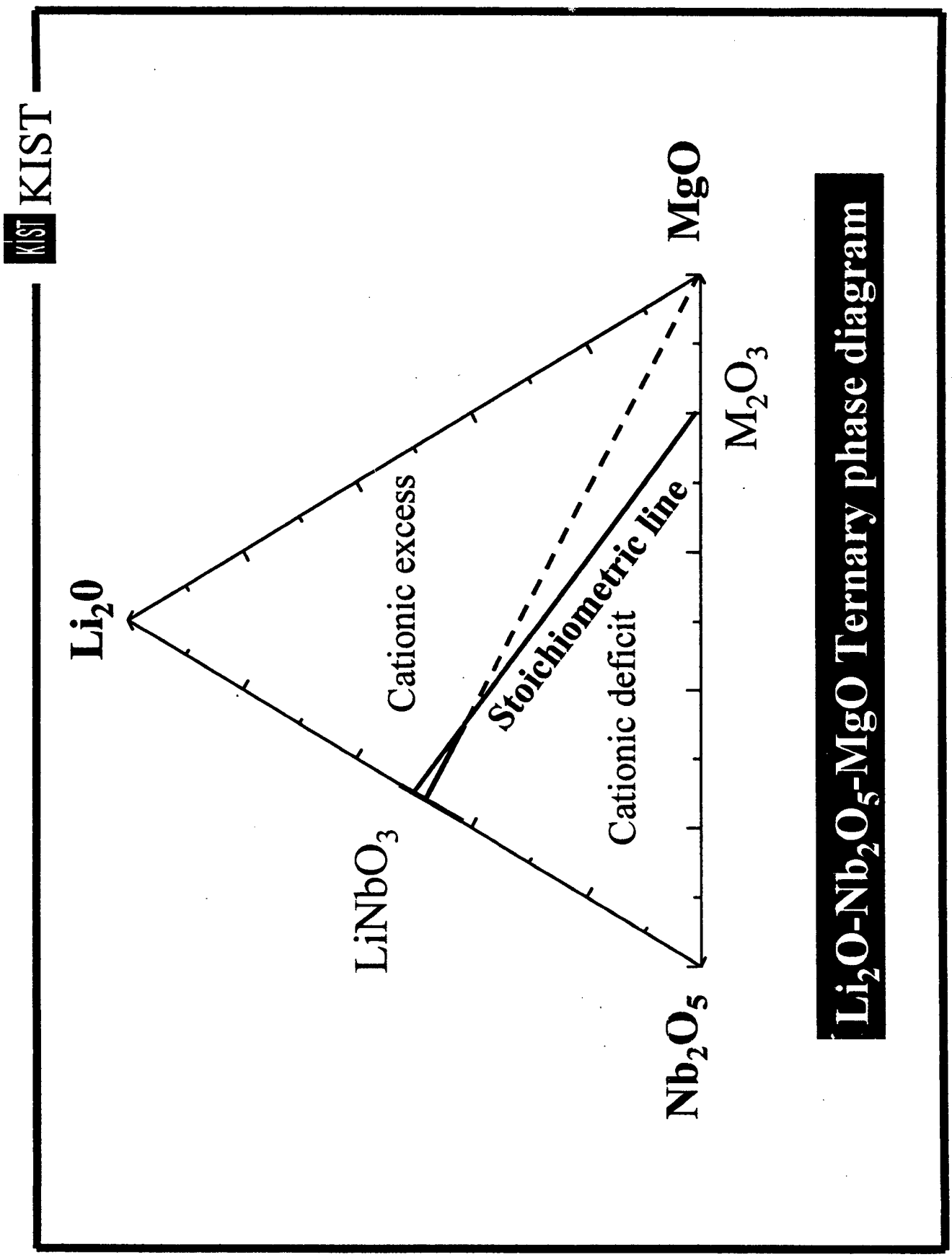
$[Li_{0.954}Nb_{0.009}\square_{0.037}][Nb]O_3$

- Ti diffusion in MgO-doped $LiNbO_3$

1) Mg ions have strong covalent bonding character with surrounding atoms

2) 3mol% MgO doping :

$[Li_{0.944}Mg_{0.030}\square_{0.026}][Nb_{0.999}\square_{0.001}]O_3$

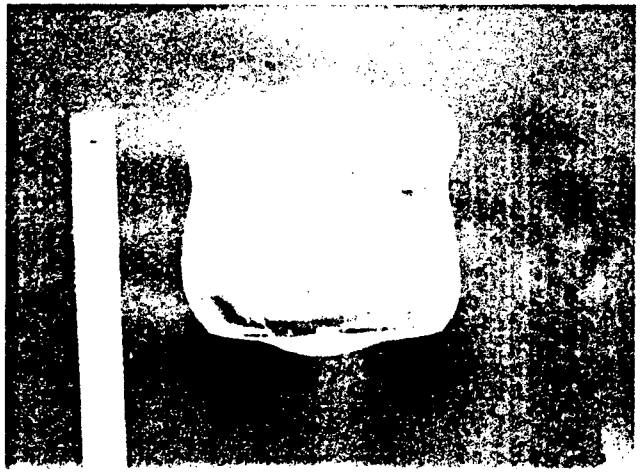

KIST
Li_2O
MgO
M_2O_3
Cationic excess
Stoichiometric line
Cationic deficit
$LiNbO_3$
Nb_2O_5
Li_2O-Nb_2O_5-MgO Ternary phase diagram

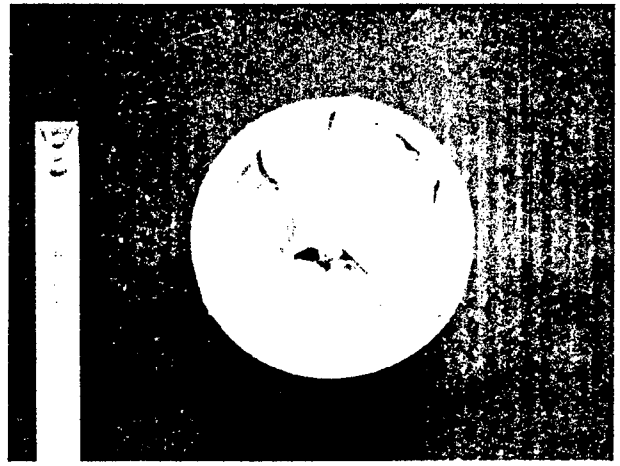
Ti diffusion into $MgO:LiNbO_3$

1. MgO mole% increase, Ti penetration depth decrease.
2. Mg ions : block for Ti in-diffusion

   for strong covalent bonding.
3. Mg accumulated layer in $LiNbO_3$: Max at 900 - 950 °C.
4. Ti in-diffusion : Gaussian equation.
5. Li out-diffusion : Error function.

ϕ 3″ $LiNbO_3$ single crystal in D company





ϕ 3'' $LiNbO_3$ single crystal