Czochralski방법에 의한 β-BaB_2O_4단결정 성장

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β-BaB_2O_4는 고출력 가시광선 및 적외선을 발진시키는데 유용한, 비선형 특성을 가진 물질이다. α-β 상전이 온도가 녹는점보다 180℃ 낮기 때문에 보통 flux법으로 단결정을 성장시킨다. 수년전 Itoh등[1]은 β-BaB_2O_4단결정을 congruent조성의 용액으로부터 Czochralski법으로 metastable한 상태에서 직접 성장시켰다. 그렇지만 그 공정은 잘 이해되지 않고 있으며 재현하기가 매우 어렵다.

저자들은 β-BaB_2O_4단결정을 용액표면온도 1035°-1085℃, pulling rate 3mm/h, 10-30 rpm의 범위에서 성장시켰으며 용액표면의 온도구배는 β-상으로 성장시키는데 매우 중요한 인자로 여겨진다. Seed로는 직경 1-2mm의 c축방향 β-BaB_2O_4단결정 봉이 사용되어 성장방향을 조절하고 열응력을 최소화시켰다. 성장된 β-상의 단결정들은 6-fold모양을 하며 표면에 작은 비늘같은 것들이 붙어있고 중심부에 core가 있는 것을 알았다. Flux법으로 성장시킨 β-BaB_2O_4단결정을 사용한 seeds는 단결정 성장 및 냉각 중에 cracks이 자주 발생하였으며, boule의 cracks은 afterheater를 사용할 경우 다소 줄일 수 있었다. 성장된 단결정의 광학특성이 측정되었다.

1) K. Itoh, F. Marumo and Y. Kuwano, "β-Barium Borate Single Crystal Grown by a Direct CzocKralsKi Method," J. Crystal Growth 106, 728 (1990).

Growth of Single Crystal β-BaB_2O_4 by the Direct Czochralski Method

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Objectives

- β-BaB_2O_4(BBO) crystals for high-power visible and UV generation
- Fast, high-yield growth process
- Improved optical quality: high crystal uniformity and elimination of scattering defects
- Low manufacturing cost process

Approach

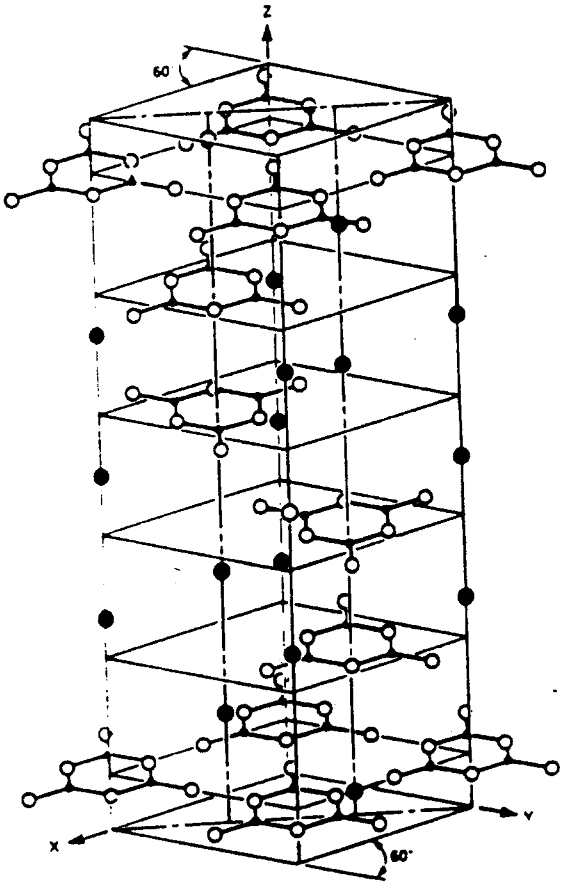
- Use metastable (derect) melt growth for 100 times faster growth rates
- Detemine thermal parameters for consistent growth of β-phase
- Eliminate the use of solvent to prevent flux inclusions and reduce optical scatter
- Develop reproducible seeding technique to maximize yield

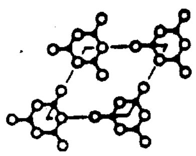
Properties of BaB_2O_4

Space group

α (high temperature) $R\bar{3}c$ (trigonal
β (low temperature) $R3c$ (trigonal

Unit cell





Thermodynamics

Melting point 1095 °C
α-β Phase transition 925 °C

Physical properties

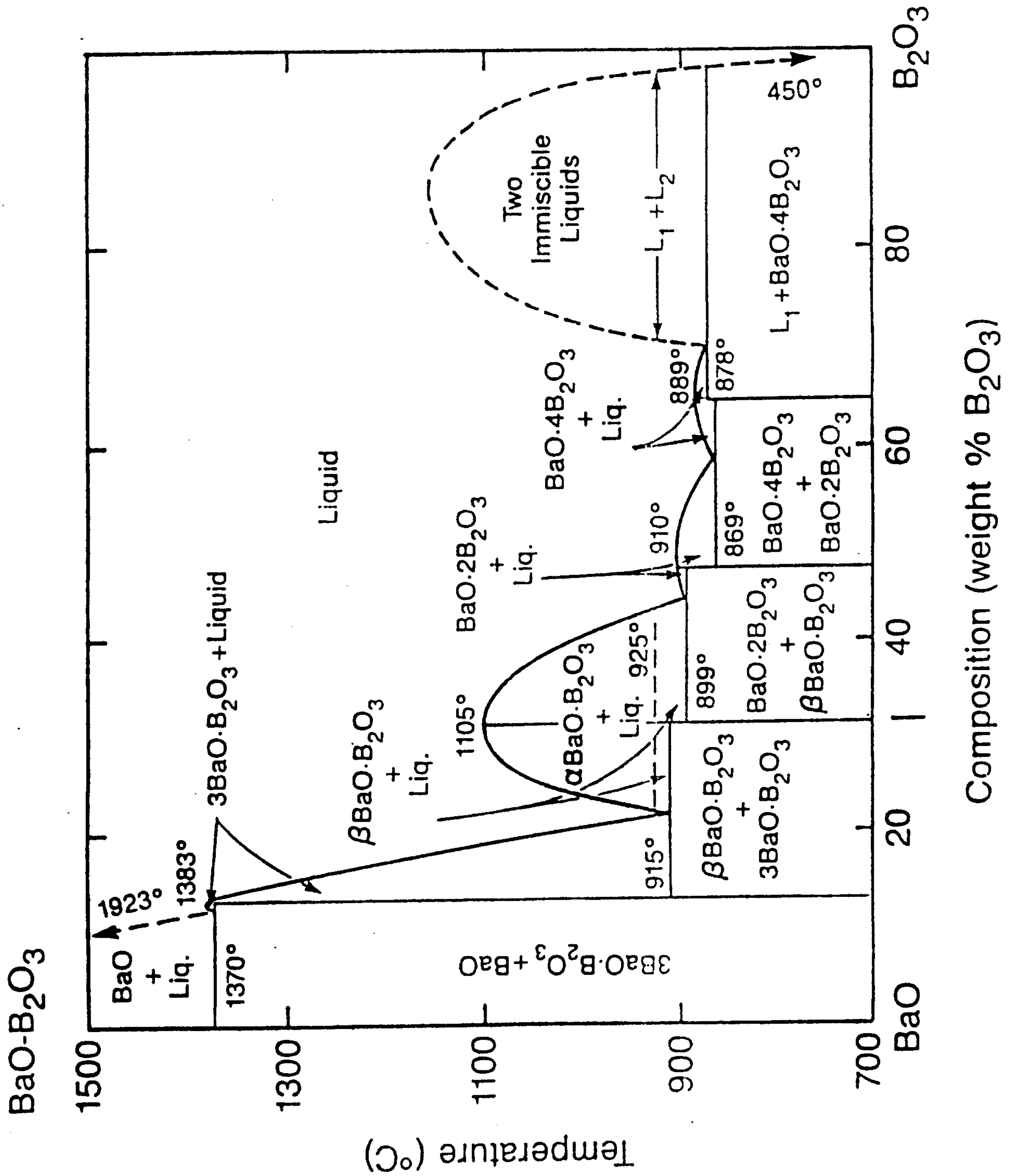
Thermal exp. coeff.
$\alpha_{11}= 4\times10^{-6}$ /°C
$\alpha_{33}=36\times10^{-6}$ /°C

Thermal conductivities
$K_{11}=0.08$ W/m °K
$K_{33}=0.8$ W/m °K

Transparency 0.190-3.50 μm

Phasematchable wavelengths (SHG)
0.205-1.50 μm

Damage threshold (λ : 1.064 μm)
- 13-15 GW/cm²


BaO-B$_2$O$_3$
1500
1300
1100
900
700
Temperature (°C)
BaO
20
40
60
80
B$_2$O$_3$
Composition (weight % B$_2$O$_3$)
Liquid
Two Immiscible Liquids
L$_1$ + L$_2$
450°
L$_1$ + BaO·4B$_2$O$_3$
BaO·4B$_2$O$_3$ + Liq.
889°
878°
BaO·4B$_2$O$_3$ + BaO·2B$_2$O$_3$
869°
910°
BaO·2B$_2$O$_3$ + Liq.
BaO·2B$_2$O$_3$ + βBaO·B$_2$O$_3$
899°
925°
αBaO·B$_2$O$_3$ + Liq.
1105°
βBaO·B$_2$O$_3$ + Liq.
βBaO·B$_2$O$_3$ + 3BaO·B$_2$O$_3$
915°
3BaO·B$_2$O$_3$ + Liquid
1383°
1923°
BaO + Liq.
1370°
3BaO·B$_2$O$_3$ + BaO

Comparison of BBO crystal growth techniques

	Solution (flux) growth	Melt growth
Advantages	- Stable growth - Strain free - Large size obtainable	- Faster pulling rate: 0.5-10 mm/h - Inclusion free
Disadvantages	- Crystal pulling rate: <1mm/day - Inclusions and light scatters - Compositional contamination due to flux	- Meta-stable growth -Strain and cracks - Restricted crystal size and growth direction

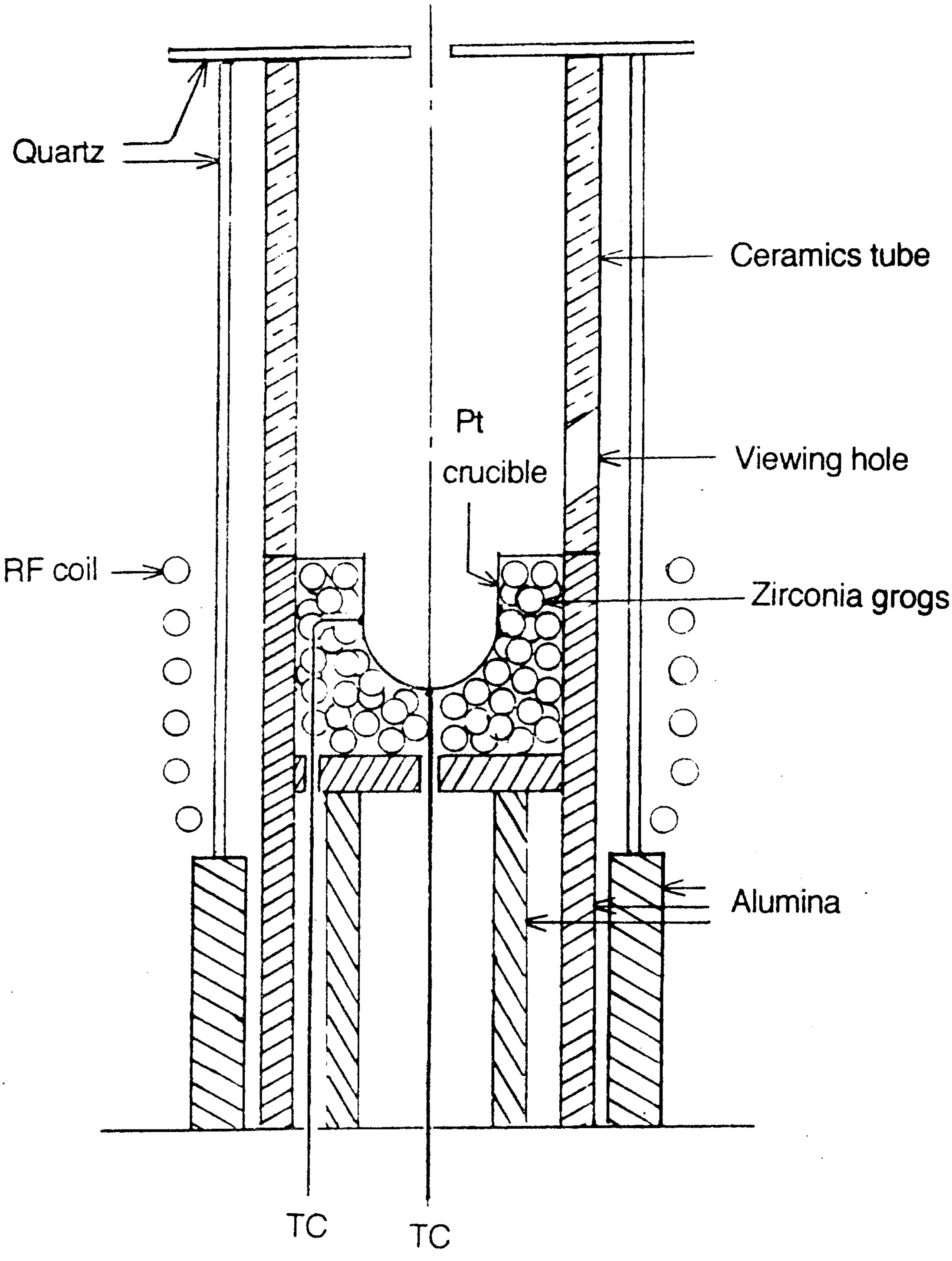
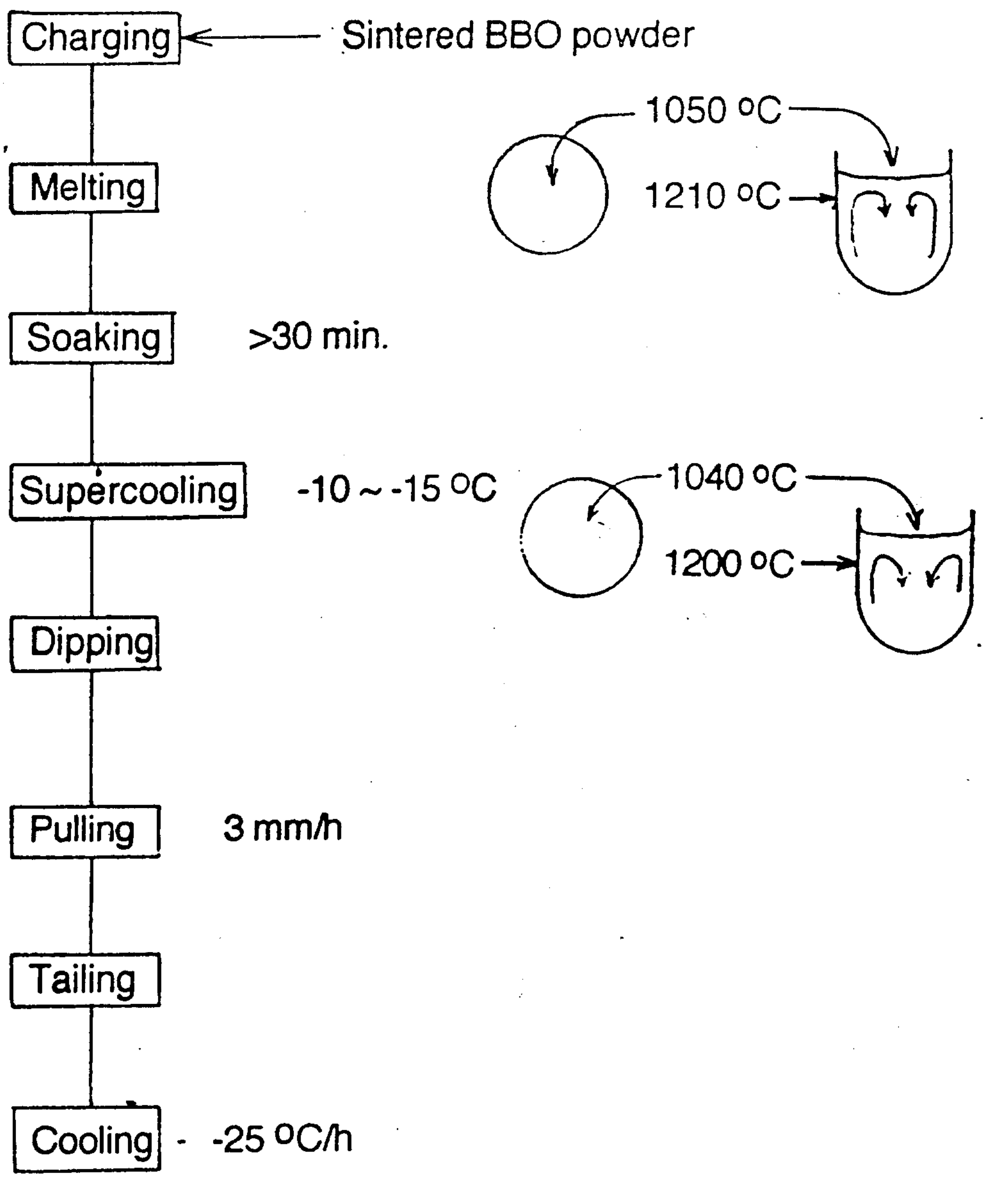


Fig. Construction of a d-CZ furnace

Flow chart of BBO crystal growth



$\frac{\Delta T}{\Delta z}_{\beta} = 34°C/mm$

$\frac{\Delta T}{\Delta z}_{\alpha} = 25°C/mm$

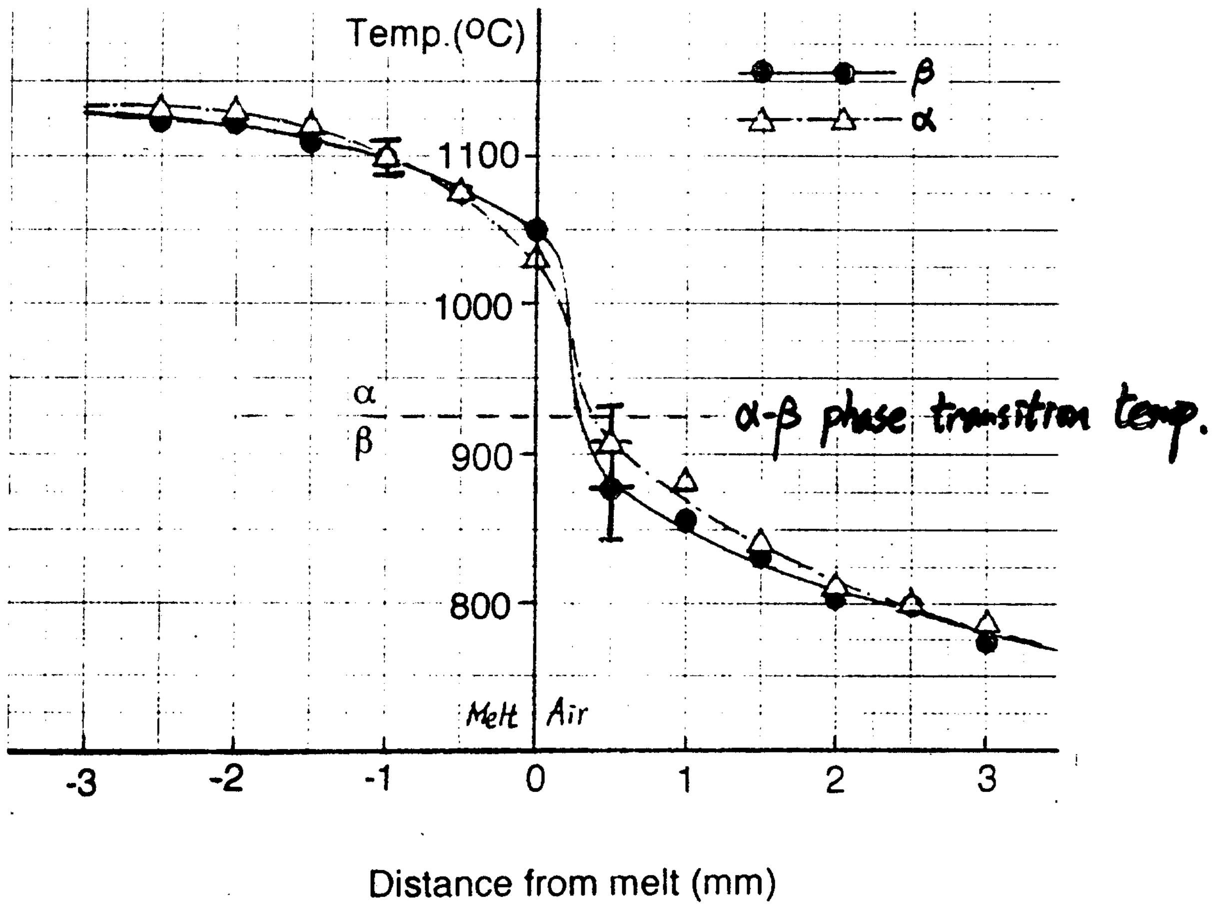


Fig. Temp. gradient near the growing point

Seeds

(1). Pt 3-wire bundle ------> mostly α-phase

(2). β-BBO crystal ---------> β-phase > α-

- size : ϕ 2~3 mm, 5~10 mm in length

Surface cracks ------> Crystal is apt to drop into melt on pulling

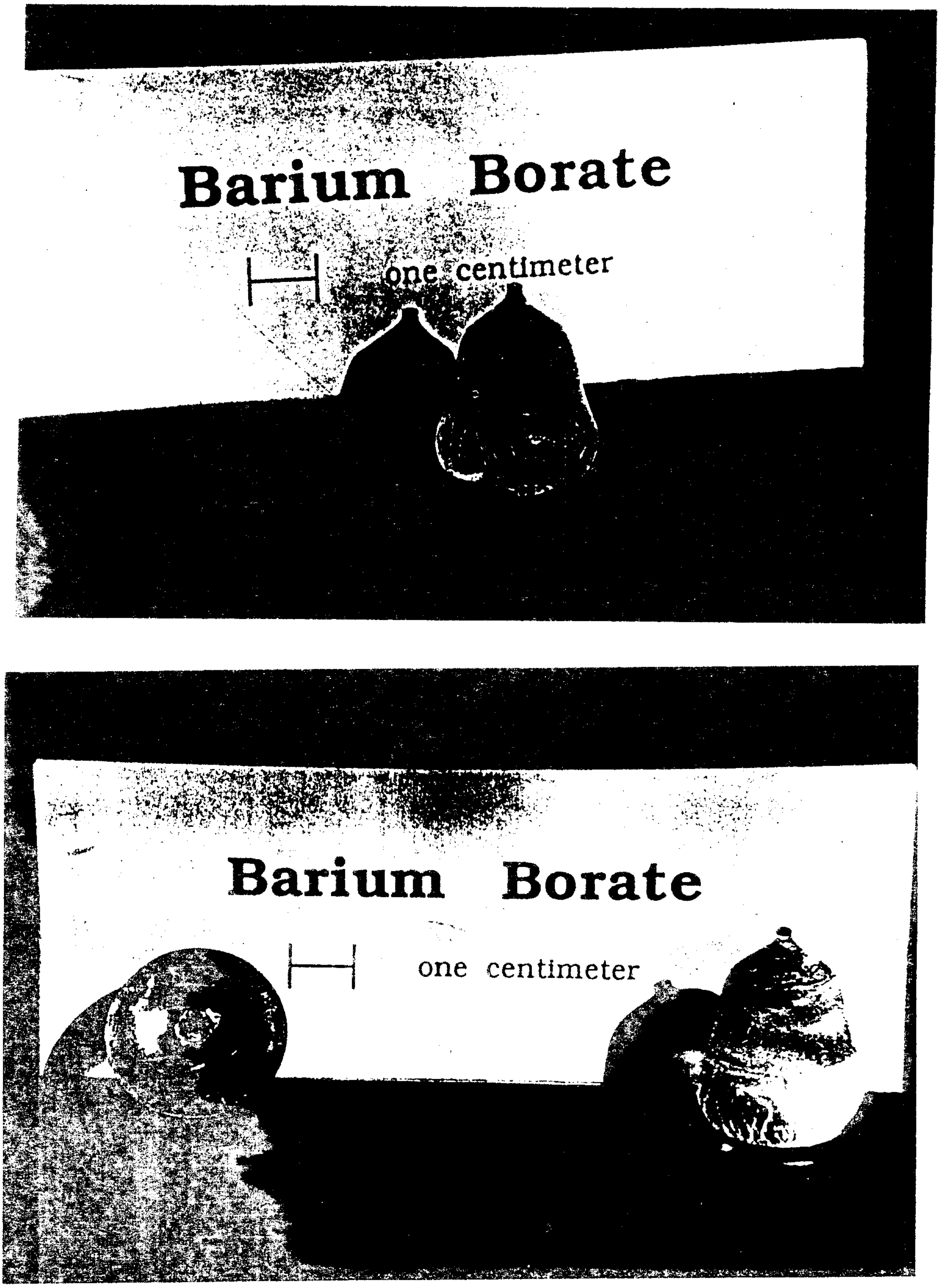
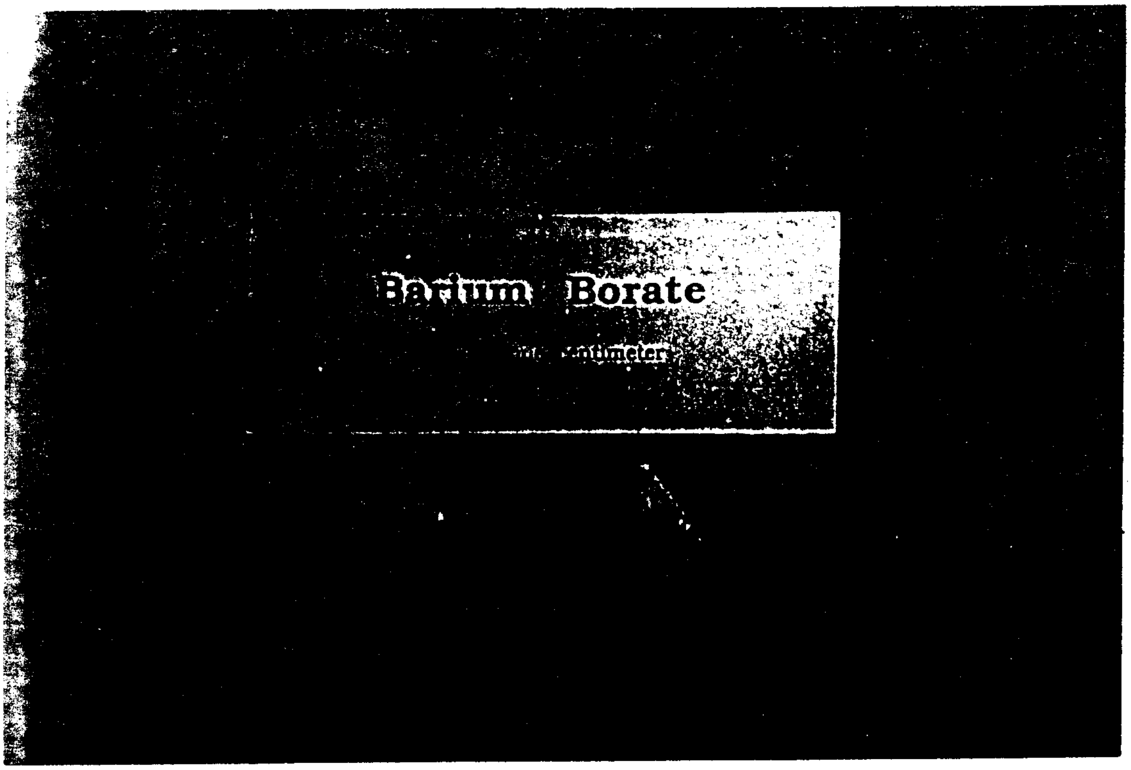


Fig. β-BBO single crystals



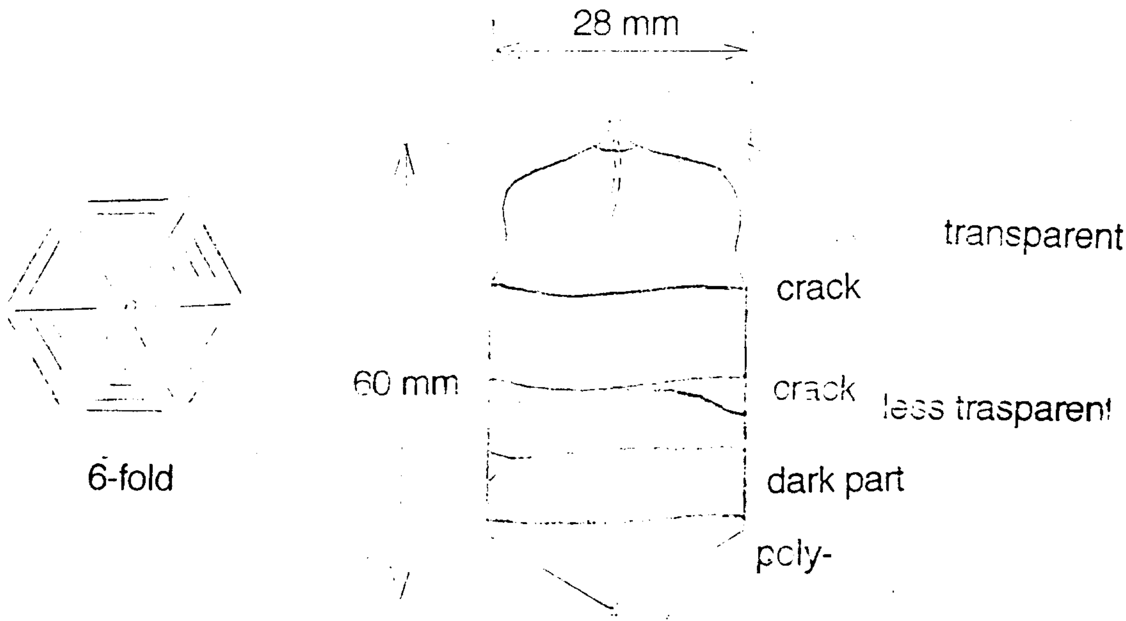
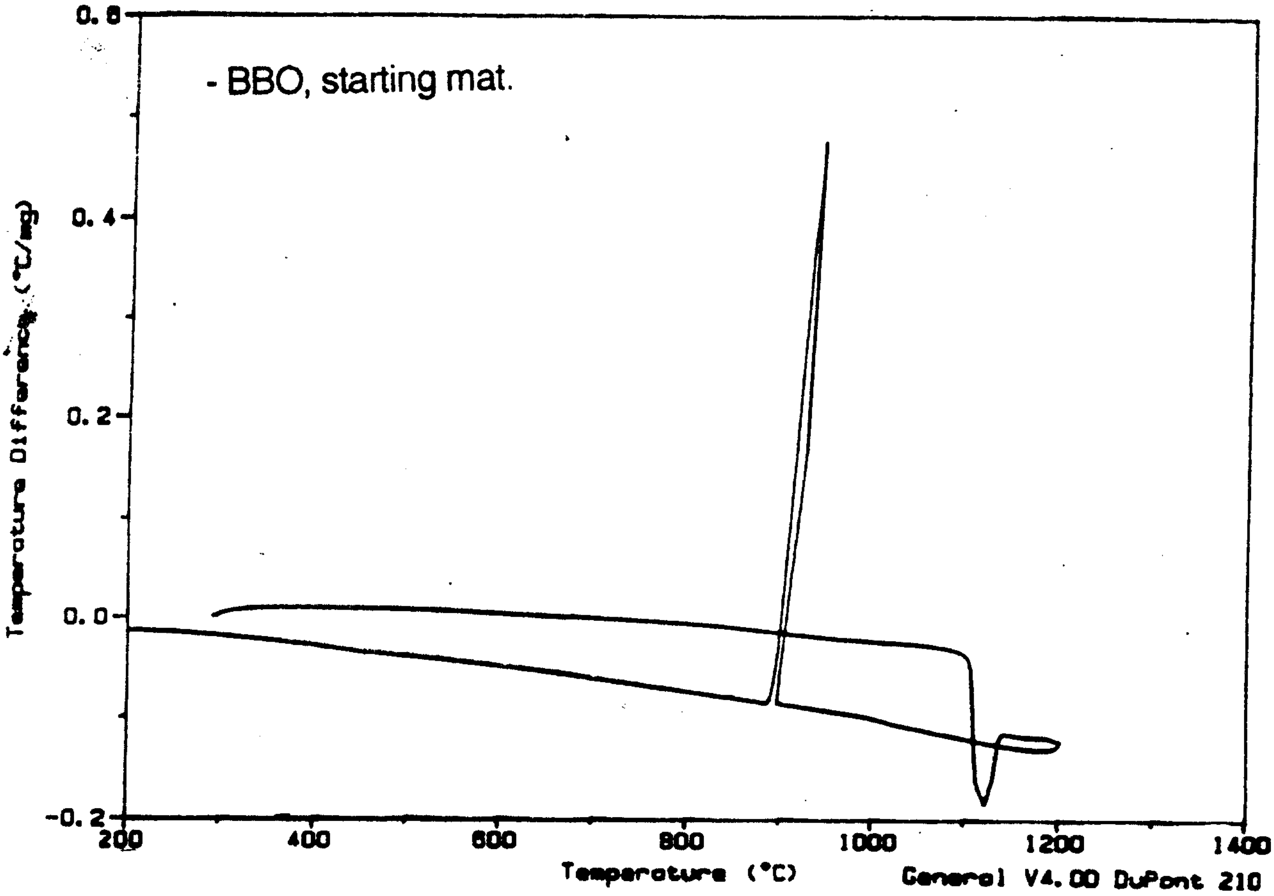


Fig. β-BBO crystal grown from the much used melt



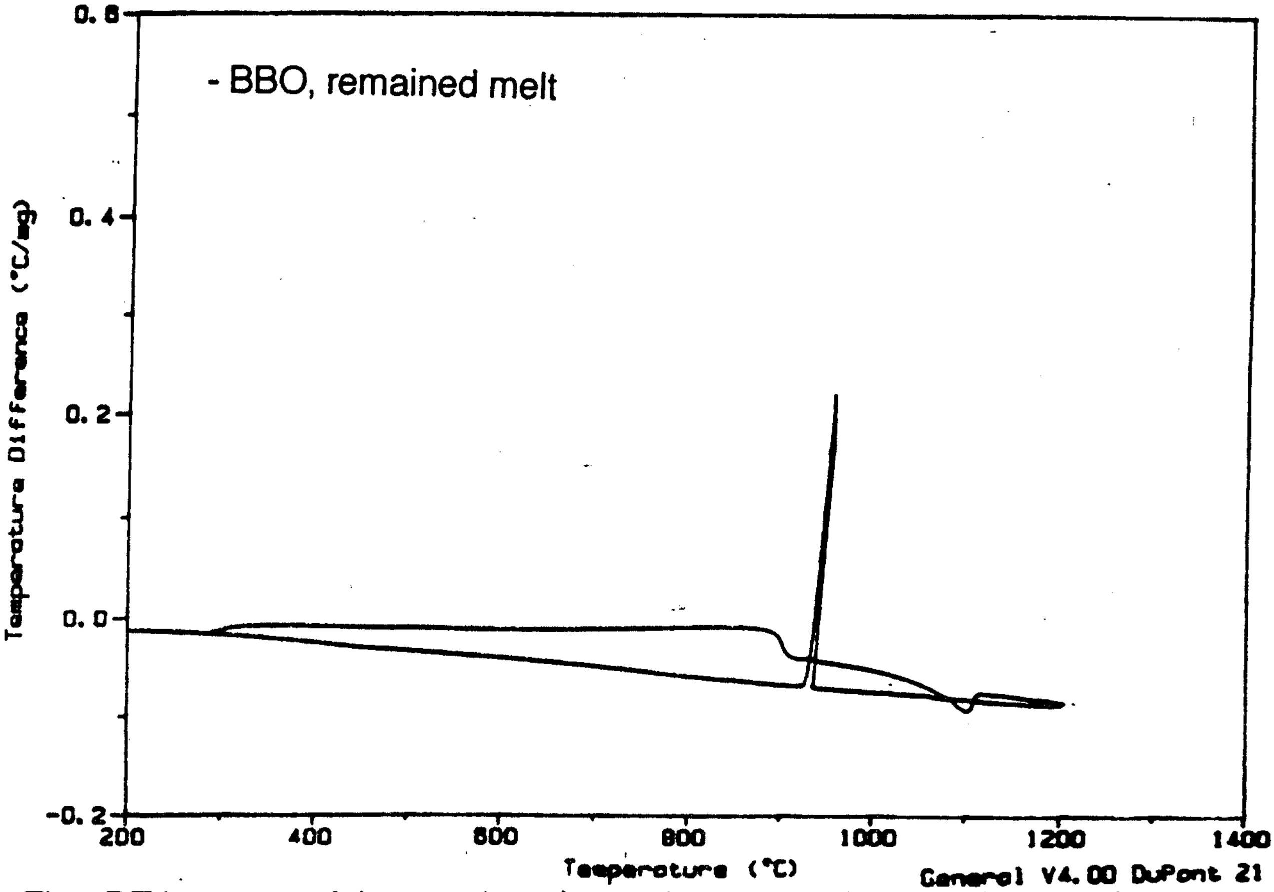
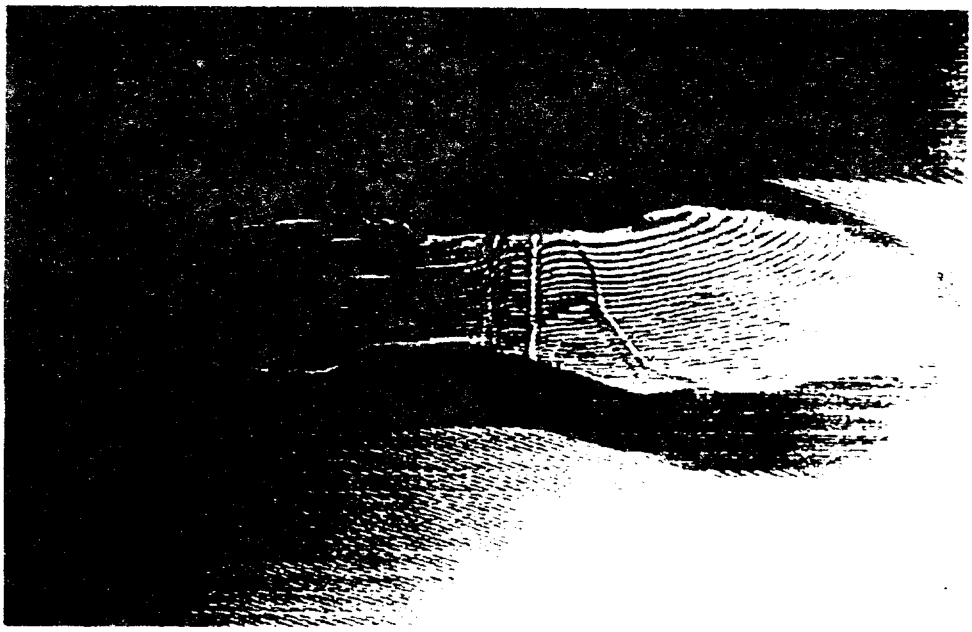
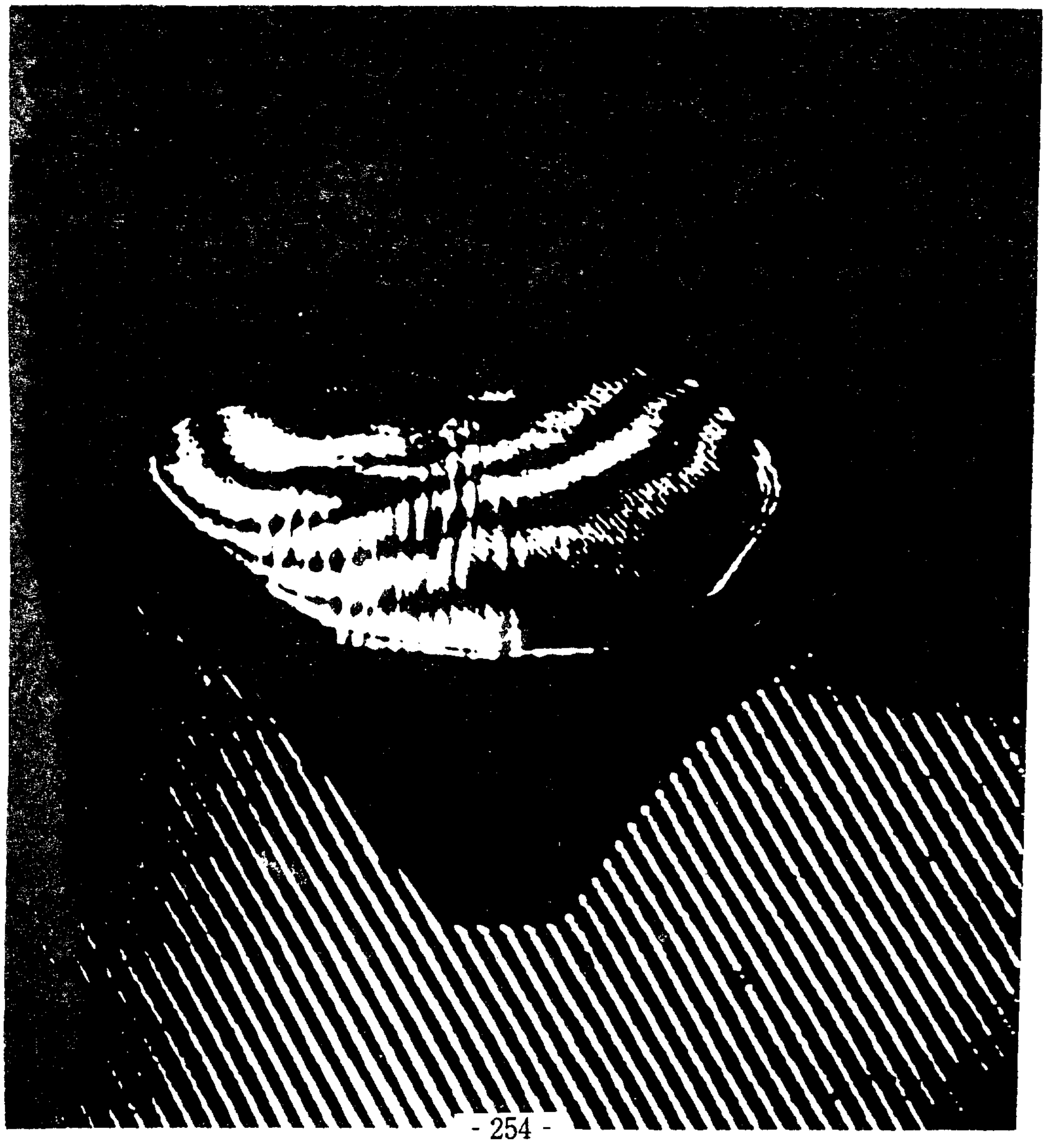
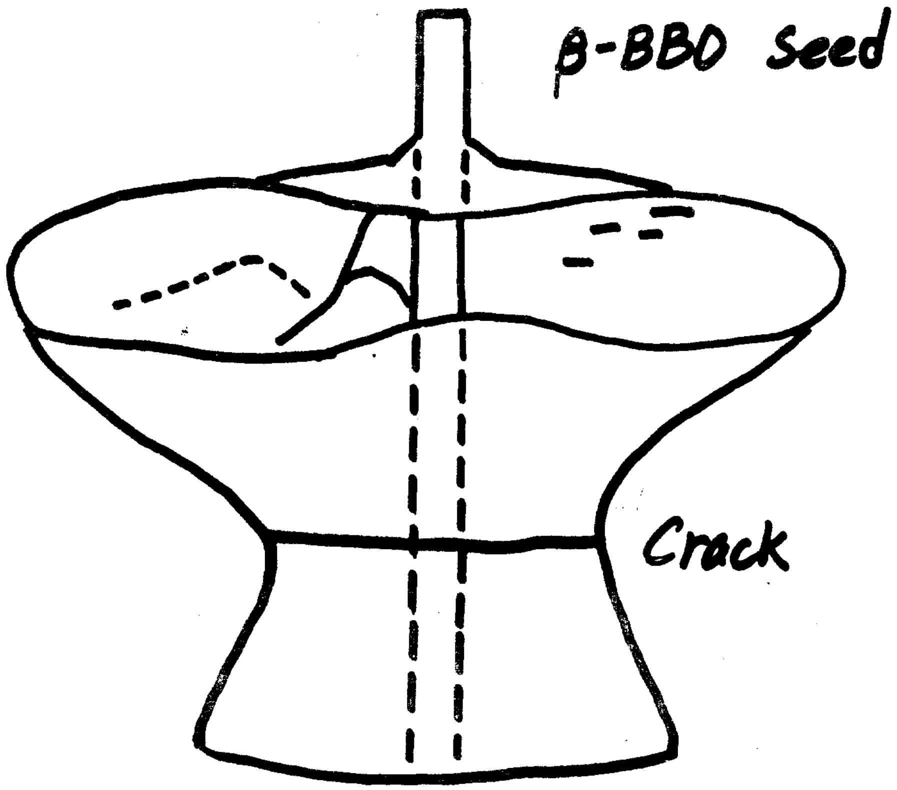
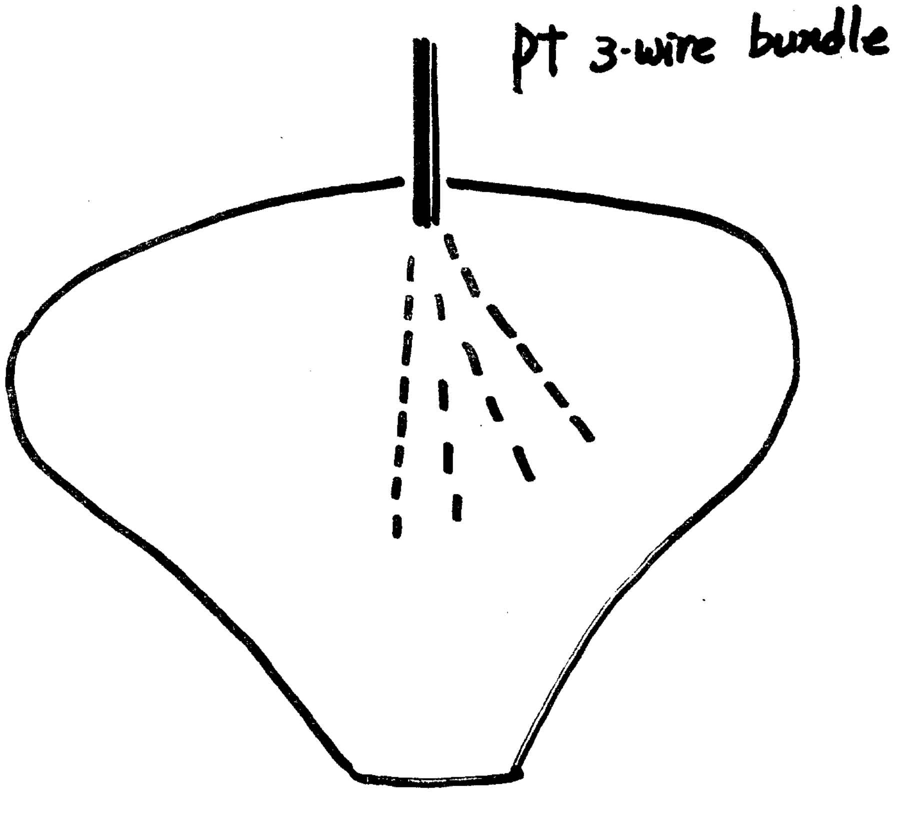


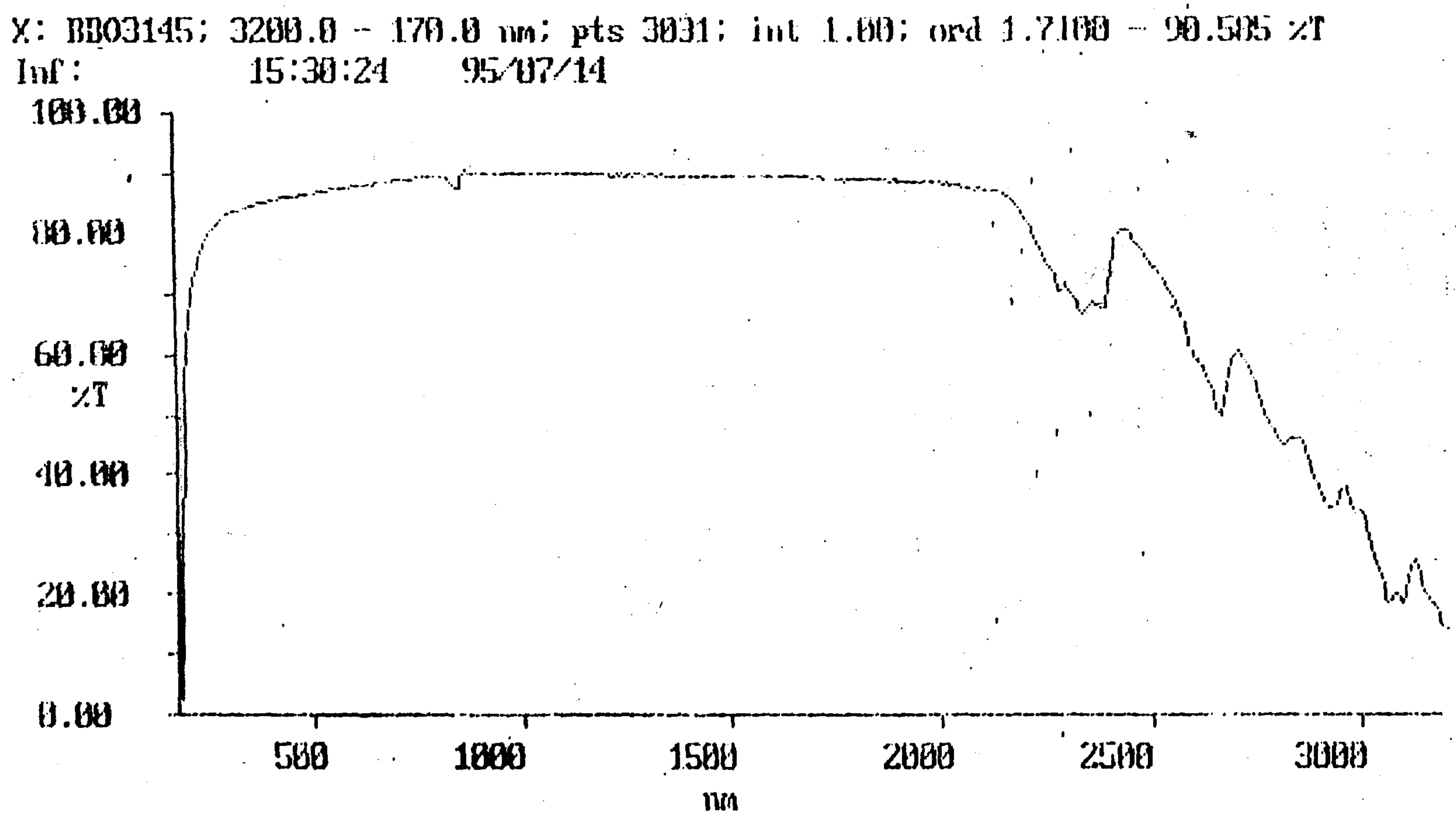
Fig. DTA curves of the starting sintered mat. and the remained melt of BBO






β-BBO Seed
Crack


Pt 3-wire bundle


X: BBO3145; 3200.0 - 170.0 nm; pts 3031; int 1.00; ord 1.7100 - 90.505 %T
Inf: 15:30:24 95/07/14
100.00
80.00
60.00
%T
40.00
20.00
0.00
500
1000
1500
2000
2500
3000
nm

Conclusions

- β-BBO single crystals, ϕ2cm, 2~4cm in length
- Large dT/dz on melt -----> β-BBO crystals
- Seed, β-BBO crystal
- Higher quality than flux grown BBO crystals

Future works

- Defects investigation
- Large size β-BBO single crystal growth
- Doped BBO crystal growth