GEM TN-92-166

BaF_2 Meeting - SSCL

August 31, 1992

Abstract:

Presentations of the GEM BaF_2 Meeting held at the SSC Laboratory on August 31, 1992.

BaF_2 Meeting Aug. 31, 1992

Transparencies

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Dr. M. Strathman, CE&A
Dr. C. Wuest , LLNL
Prof. H. Newman . Caltech
Dr. R.Y. Zhu , Caltech
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PROGRESS ON BaF_2 R&D IN SIC

Z. W. YIN

August 20, 1992

SHANGHAI INSTITUTE OF CERAMICS
CHINESE ACADEMY OF SCIENCES

Experiment of BaF_2 Crystal Growth

1. Test of Raw Materials from Different Vendors

The effect of barium fluoride raw materials produced by different vendors on the quality of crystals has been investigated. The vendors are:

- Sha-gang Chemical Works, Haian County, Jiangsu Province (Haian)
- Yong-kang Chemical Works, Jinhua City, Zhejiang Province (YKCW)
- Beijing General Chemical Works (BGCW)
- School-run workshop of Beihai Middle School, Shanghai (Beihai)

Table 1 Cation impurities in raw materials (wt.ppm) analyzed with Atomic Absorption Spectroscopy.

	Haian	YKCW	BGCW	Beihai
Fe	2.5	3.0	2.0	2.0
Co	0.4	0.5	0.3	0.3
Mn	0.1	0.1	0.4	<0.1
Ni	1.0	0.7	3.0	1.0
Cr	—	0.6	2.0	1.0
Pb	0.55	0.5	0.2	0.2
Ca	0.35	0.2	5.0	0.6
Mg	1.0	2.0	0.4	30
Sr	300	83	46700	700

- No rear-earth impurities were detected in these raw materials
- Sr content in BGCW raw material is greater than that in the others by a factor of 2 orders
- Mg content in Beihai raw material is 30 times greater than that in the others
- The contents of the other impurities in raw materials from these four vendors are similar to each other

Fig. 1 shows the transmission spectra before and 20 hours after 1 MRad ^{60}Co gamma ray irradiation for crystals produced under the same condition using raw materials from the above four vendors.

Fig. 2 and Fig. 3 demonstrate the transmission spectra after irradiation of the crystals which were grown under different conditions with the different batches of raw materials of Haian and YKCW respectively. These figures show:

- In spite of the different transmitting lengths of crystals, the one grown with Haian raw material has the best radiation hardness.

- Although the transmission spectra after irradiation are numerically different for crystals grown with the same raw material, the configurations of the curves are essentially identical.

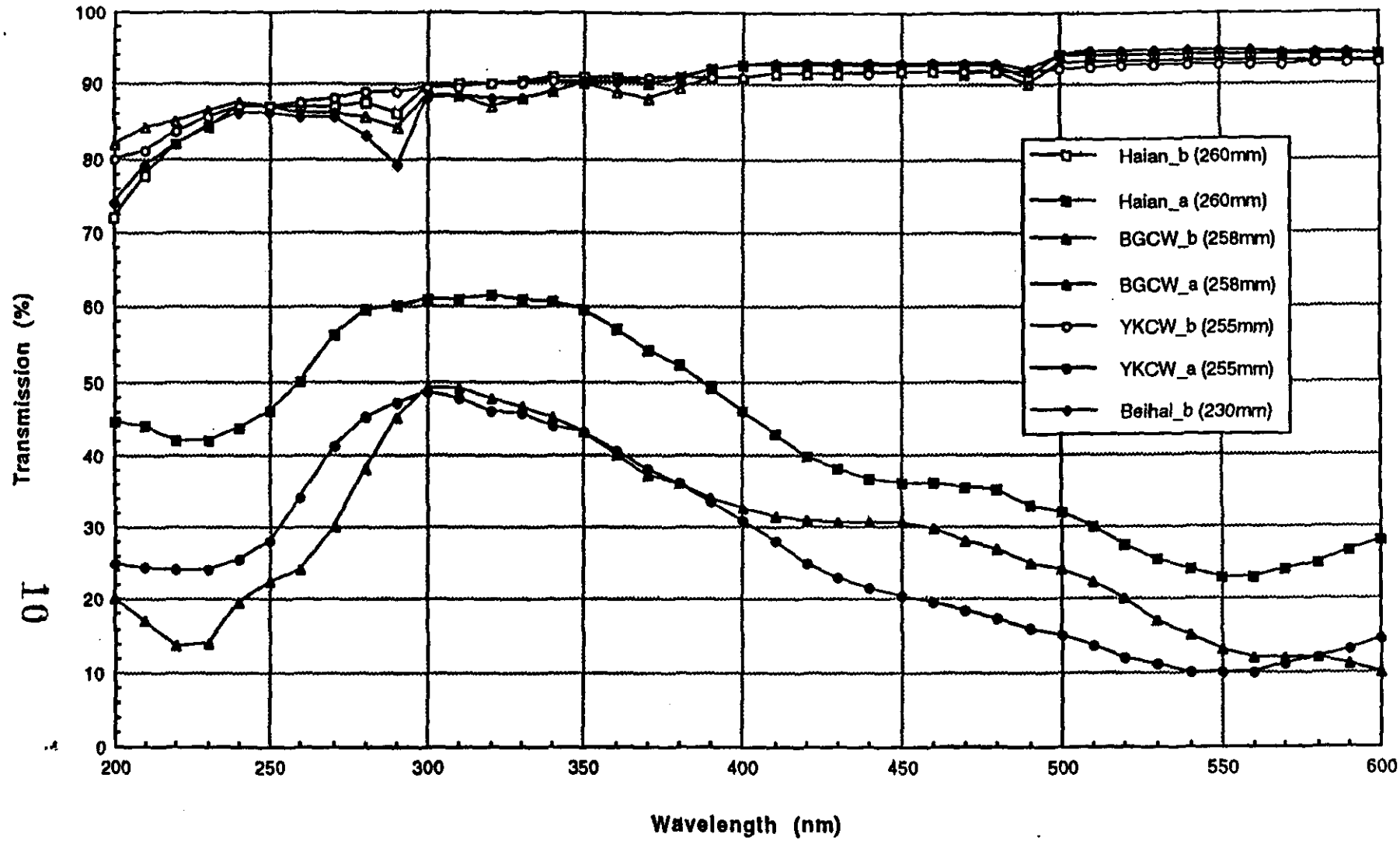


Fig.1 Transiossion spectra before and 20 hrs after irradiation for crystal produced under the same condition with the raw matericals from four vendors

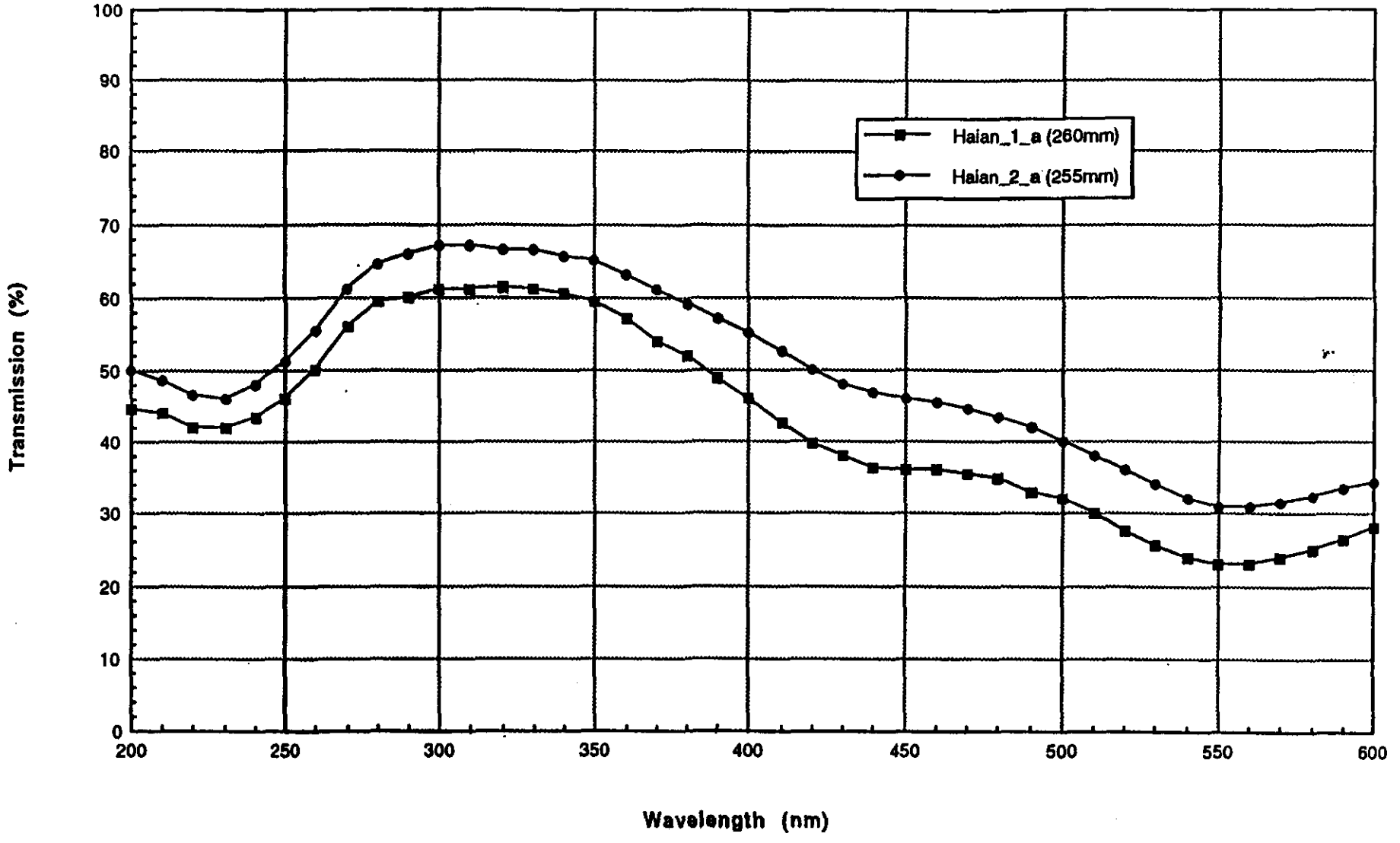


Fig.2 Transmission spectra after irradiation of the crystal grown under different condition with different batches of Halan raw materical

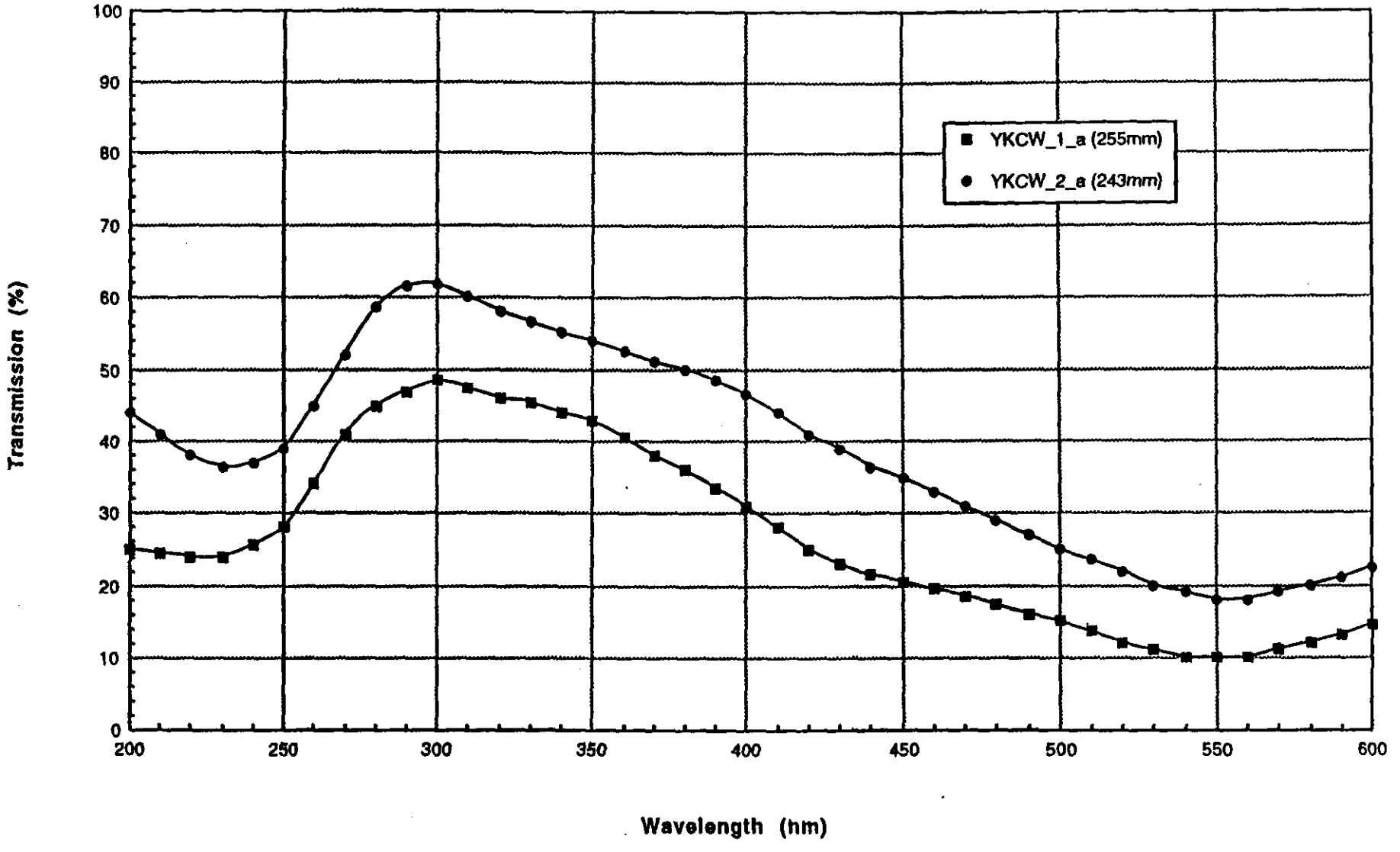


Fig.3 Transmission spectra after irradiation of the crystal grown under different condition with different batches of YKCW raw materical

2. Annealing Test

The effect of annealing process on radiation hardness of large size BaF_2 crystal after irradiation was studied.

- Crystal grown with Haian raw material
- Crystal size: (3x3) x 26 x (4x4) cm^3
- Irradiating before annealing: 1 MRad ^{60}Co gamma ray
- Annealing condition: $500^{o}C$ under high vacuum for four hours, then slow cooling to room temperature
- Lapping and re-polishing of the two ends of the crystal, with the total length reduced from 260 to 257mm
- Irradiating the annealed crystal again with ^{60}Co, 1 MRad

Fig. 4 shows that the measured transmission spectra of the crystal before and after annealing coincided very well.

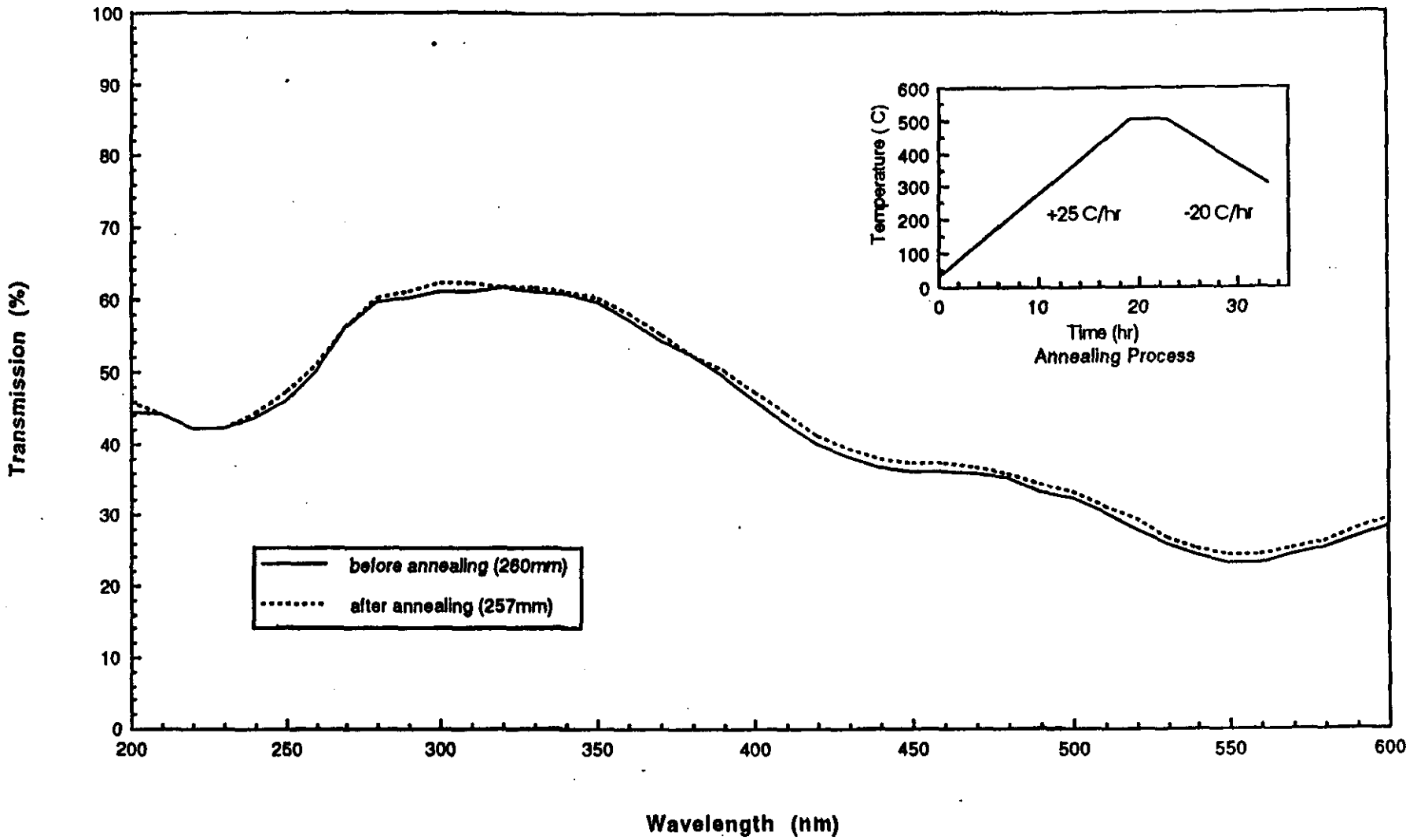


Fig.4 Transmission spectra of irradiated crystal before and after annealing process

3. Improvement on the Vacuum System of Growth Furnace

- A set of liquid nitrogen cooling trap was designed and manufactured by *Shanghai Institute of General Machinery* and installed onto growth furnace in the early June of 1992

- Under the case of unheating and non-loading, the vacuum in the furnace was 3.6×10^{-3} Pa before the liquid nitrogen being injected,and down to 6×10^{-4} Pa after infected,that means the system has fulfilled the design requirements

- For the time being, the comparative experiments of crystal growth are under way with and without the cooling trap

- The leak-up-rate test was carried out with No.1 growth furnace at room temperature. The result indicated that its leak up rate was less than that of normal vacuum system, i.e., 10^{-6} Torr/sec

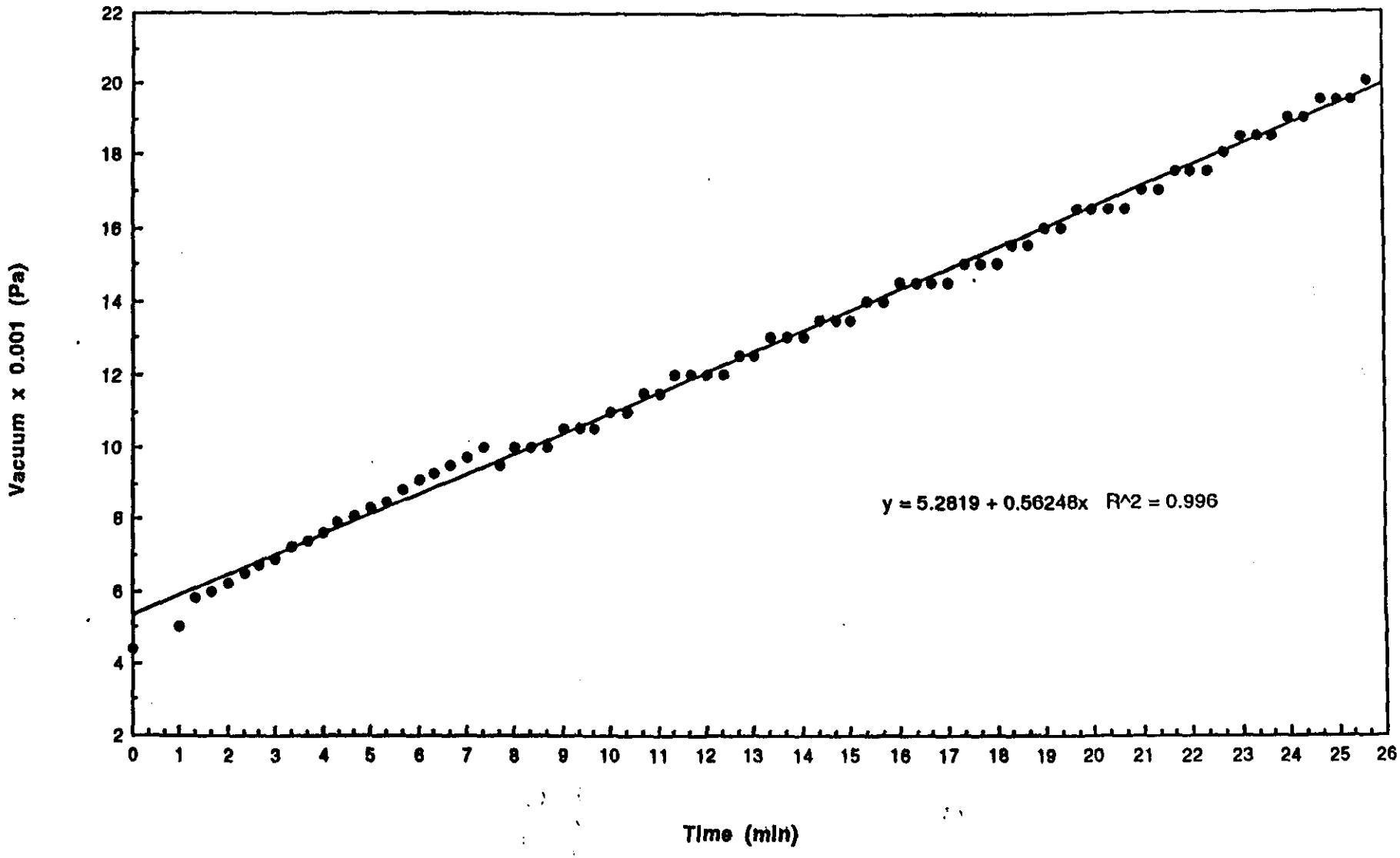


Fig.5 Leak-up rate of growth furnace No.1 at room temperature

Investigation on Mechanism of Radiation Damage

1. Effect of OH^- on Radiation Damage in Barium Fluoride†

By the theory of *Localized Spin-state Density* (LSD), the electronic structures of the impurities in BaF_2 crystal have been calculated and the location of absorption peaks caused by color centers, hydroxyl and oxygen impurity centers were determined. In the mean time, transmission spectra of BaF_2 sample with and without heat treatment of $900^{\circ}C$ in atmosphere (70% R.H.) were measured under the condition of vacuum ultra-violet, UV and IR.

†This work was carried out by *Pohl Institute of Solid State Physics*, Tongji University, Shanghai.

- Sample: **JB1-9112 (Haian)**

- Hydrolytic process during crystal growth or treatment:

$$BaF_2 + 2H_2O \longrightarrow Ba(OH)_2 + 2HF$$

OH^-: 192nm

- Radiolytic process during irradiation:

$$OH^- \longrightarrow H_i^o + O_s^- \qquad or$$

$$\longrightarrow H_s^- (U) + O_i^o$$

U: 204nm
793.75cm^{-1} in IR absorption spectrum

O_s^-: ~240nm

Fig.6, 7 and 8 show that the wavelengths of the absorption peaks appeared in the spectra corresponding to those arisen from the hydroxyl and the oxygen impurities introduced by the hydrolytic and the radiolytic process of BaF_2 crystal. Thus it may be considered that the restraint of hydrolysis of BaF_2 crystal will enable its radiation hardness to be improved or controlled.

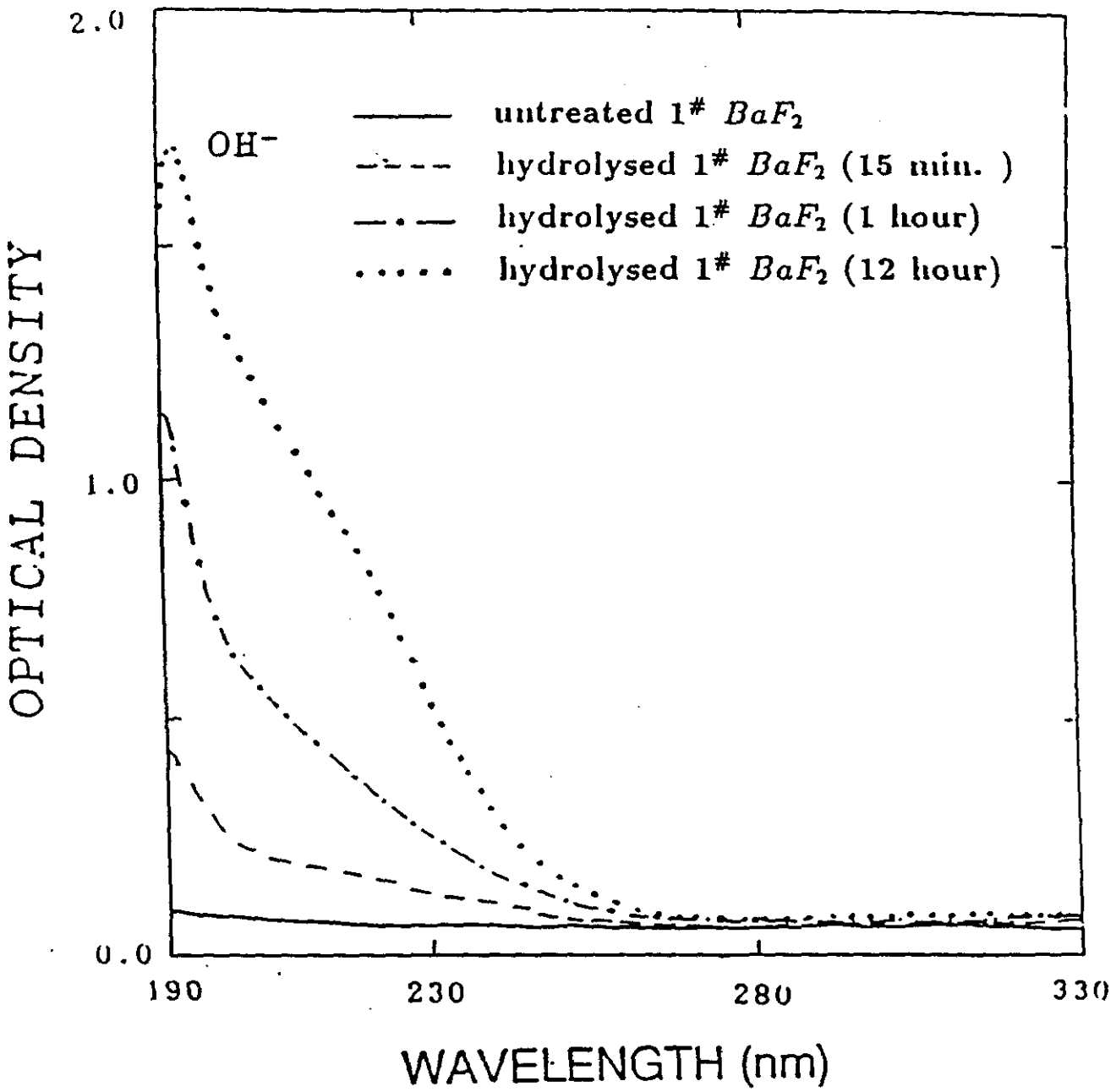


Fig. 6. Absorption spectra for different hydrolysed 1# BaF_2

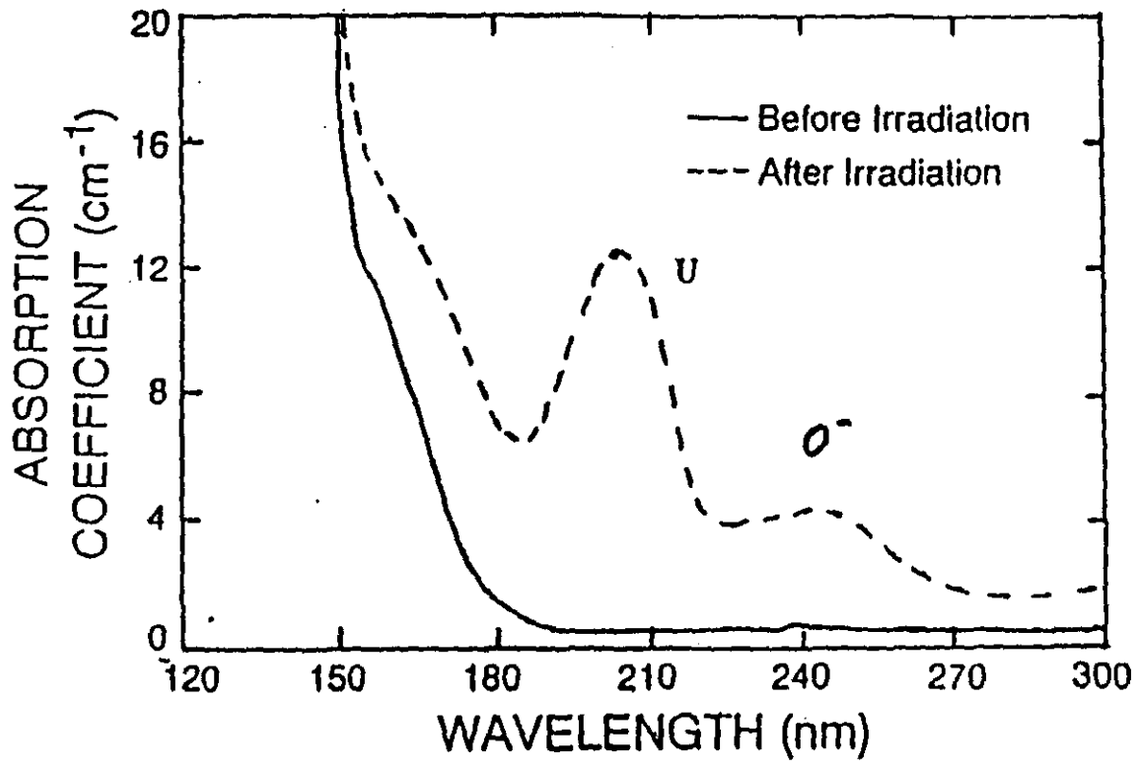


Fig. 7. Absorption spectra of hydrolysed 1# BaF_2 before and after irradiation

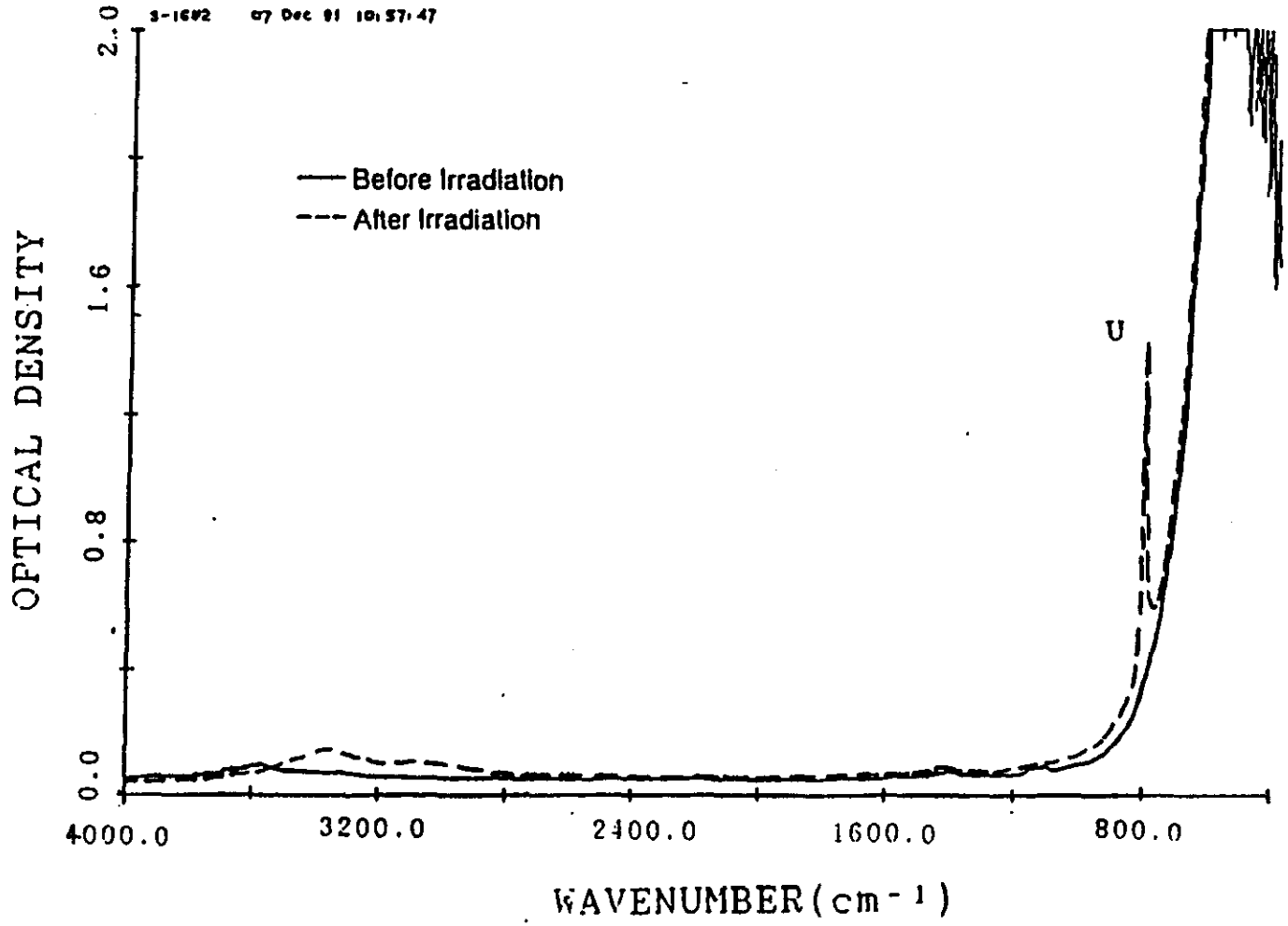


Fig. 8. IR Absorption spectra for hydrolysed 1# BaF_2 before and after irradiation

2. Electron Diffraction Study

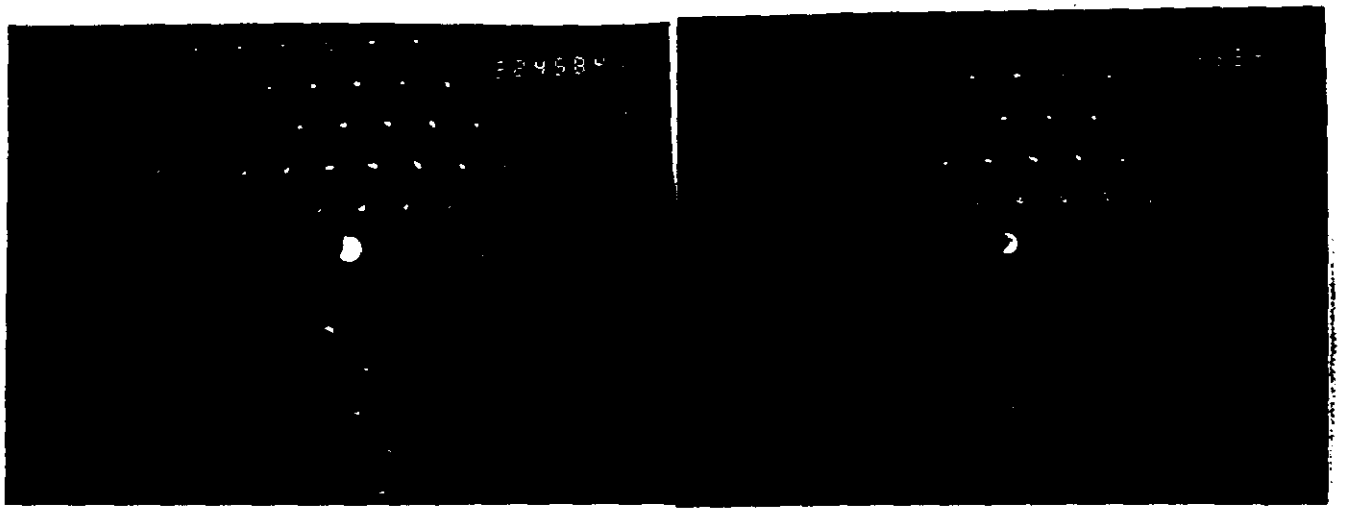
This work was to study the change of electron diffraction pattern after the electron bombardment. The experimental condition was:

- 200 kV, 20~30μA and vacuum of 10^{-7} Torr
- BaF_2 crystal was ground to powder with particle size of ø0.1~1μm
- Electron beam of diameter of 1000A was focused onto the BaF_2 powder
- Two pictures were taken: one at the beginning of bombardment and the other after two minutes of bombardment.
- Different BaF_2 crystal samples labeled as No.1, 2 and 3 were powdered. The amount of oxygen content was:

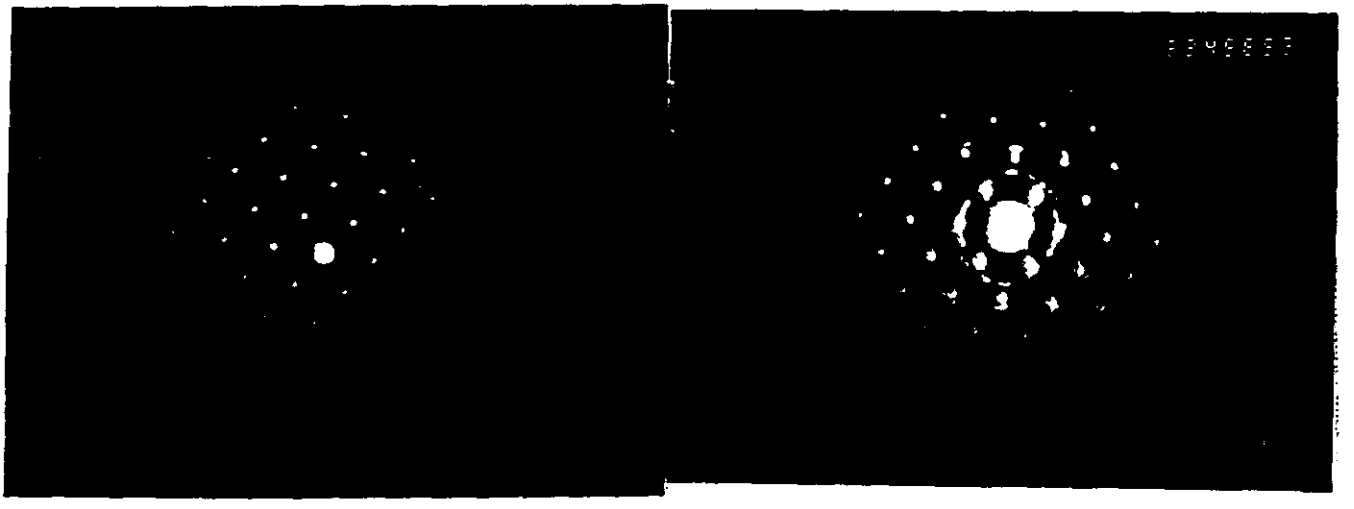
  No.2 > No.3 > No.1

  However, No.3 was a fast cooling sample, that means there were more imperfections in its crystal structure.

Fig.9 Change of electron diffraction pattern of three different BaF_2 crystal samples at the beginning and after two minutes of electron bombardment. The transmission of 25cm long crystal at 220nm after 10^6 Rad ^{60}Co irradiation of the above three crystal samples were 42% (No.1), 25% (No.2) and <5% (No.3) respectively. In the patterns, the regular spots belong to BaF_2 lattice, rings and extra spots belong to BaO lattice. Halo in No.3 pattern shows that after two minutes of electron bombardment, crystal transformed into glassy state.



No. 1



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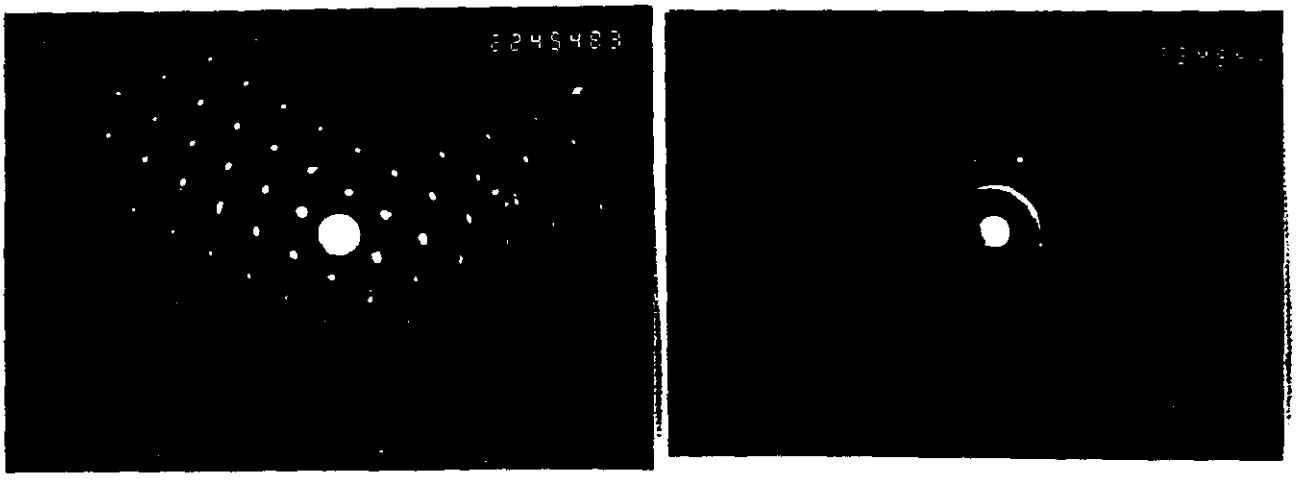


No. 3

3. Electron Energy Loss Spectrum Study

- Instrument: Phillips CM-12 Analytical Electron Microscope (AEM)

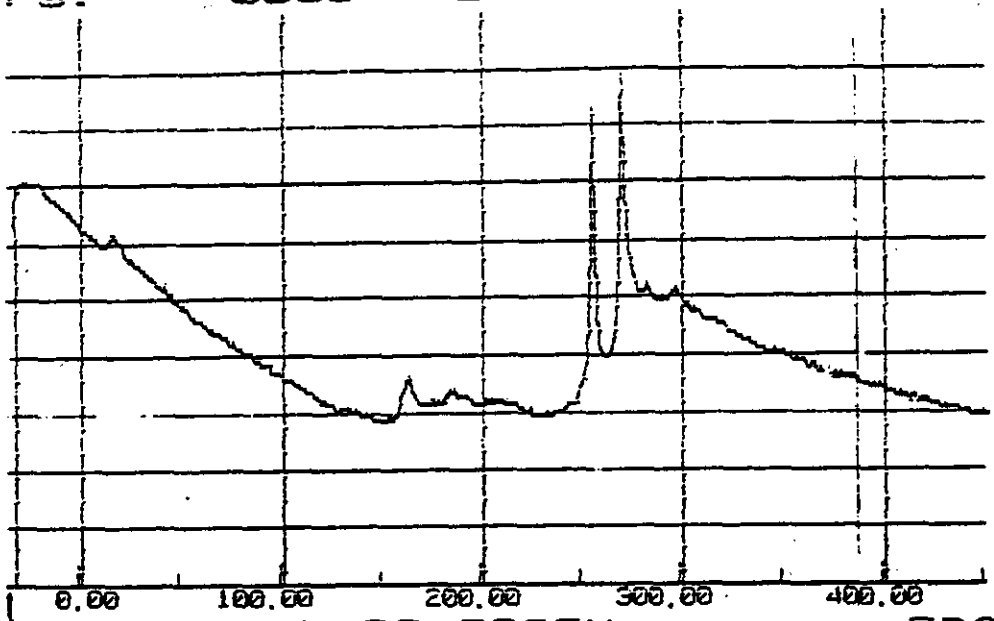
- Functions: TEM + EDS + PEELS
  PEELS (Parallel Electron Energy Loss Spectrum)
  —— Gatan 666, USA

- Experimental condition: 100kV, 20μA

- Samples: same as for electron diffraction study

- Two curves were taken for each sample: one at the beginning of bombardment and the other after twenty minutes of bombardment.

13-JUL-92 14:23:29 EELS/PD
SCAN 1 OF 0DWELL:800.000MSEC
OFFSET= -34.50EV/CH= 0.5000
LBL:
FS: 3368 MEM: A CNT: 2341



MODE:Refresh/Normal -32.500EV EDAX

13-JUL-92 14:31:30 EELS/PD
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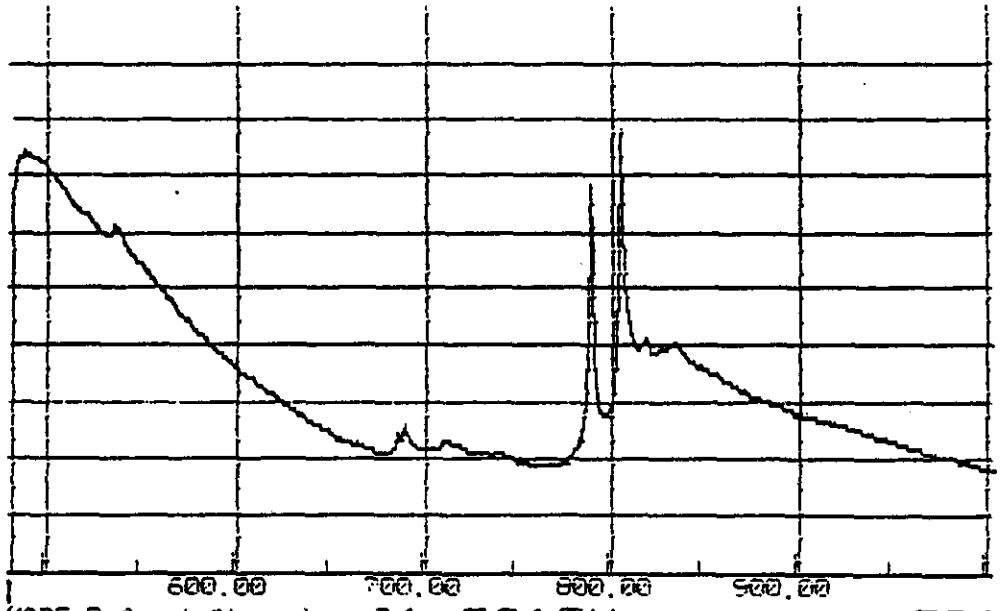
LBL:
FS: 3368 MEM: A CNT: 2265



MODE:Refresh/Normal 31.561EV EDAX

No. 1

13-JUL-92 14:40:05 EELS/PD
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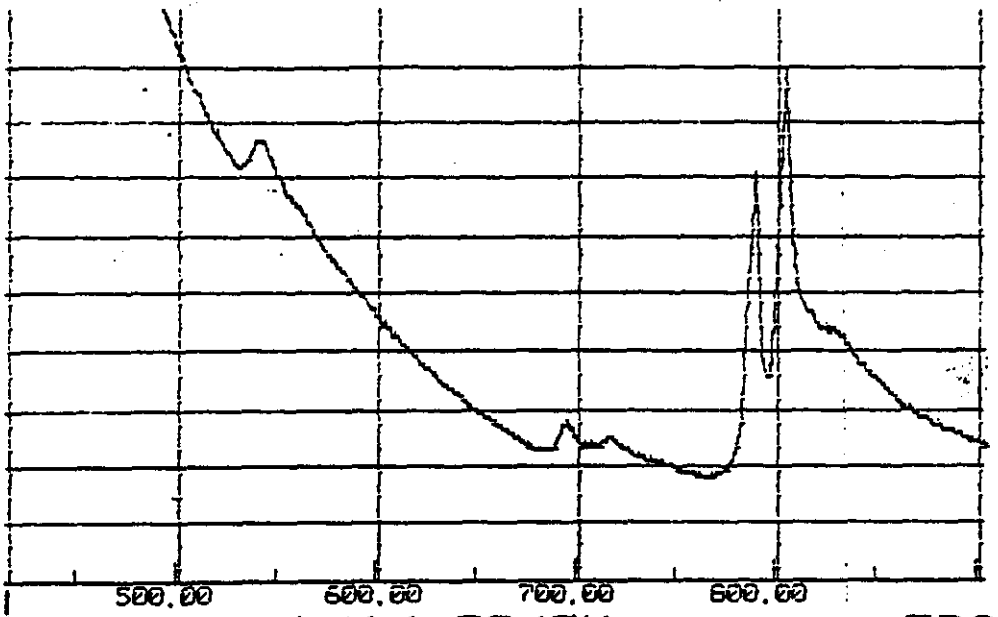
LBL:
FS: 4142 MEM: B CNT: 6760



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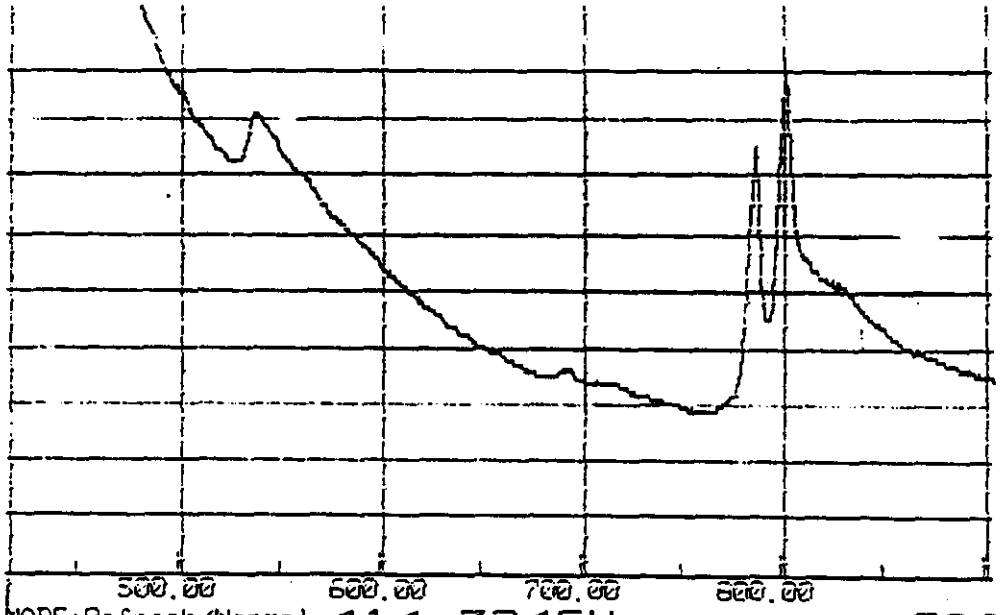
LBL:
FS: 4142 MEM: A CNT: 5655



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LBL:
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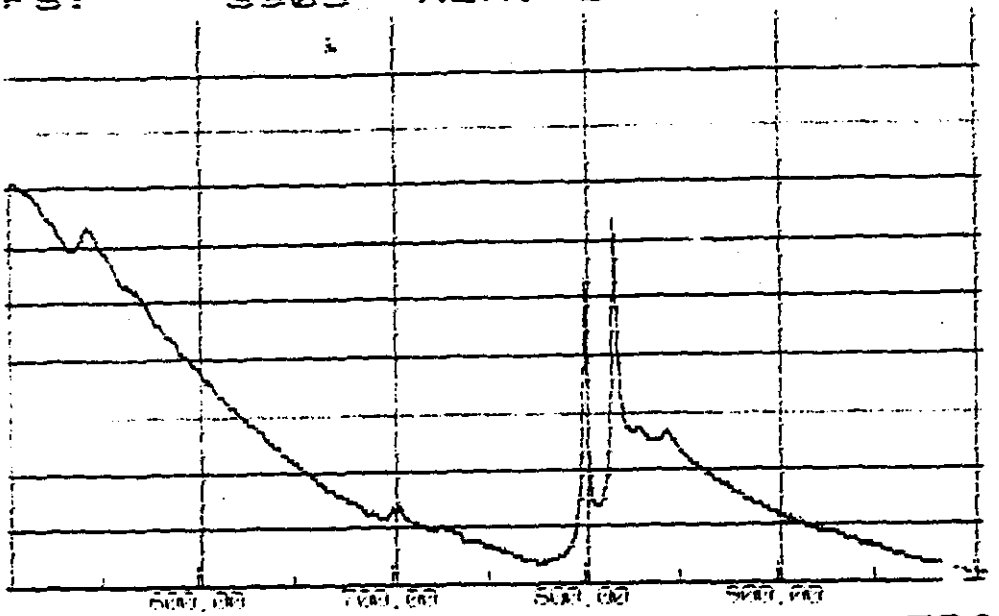

MODE:Refresh/Normal 500.358EV EDAX

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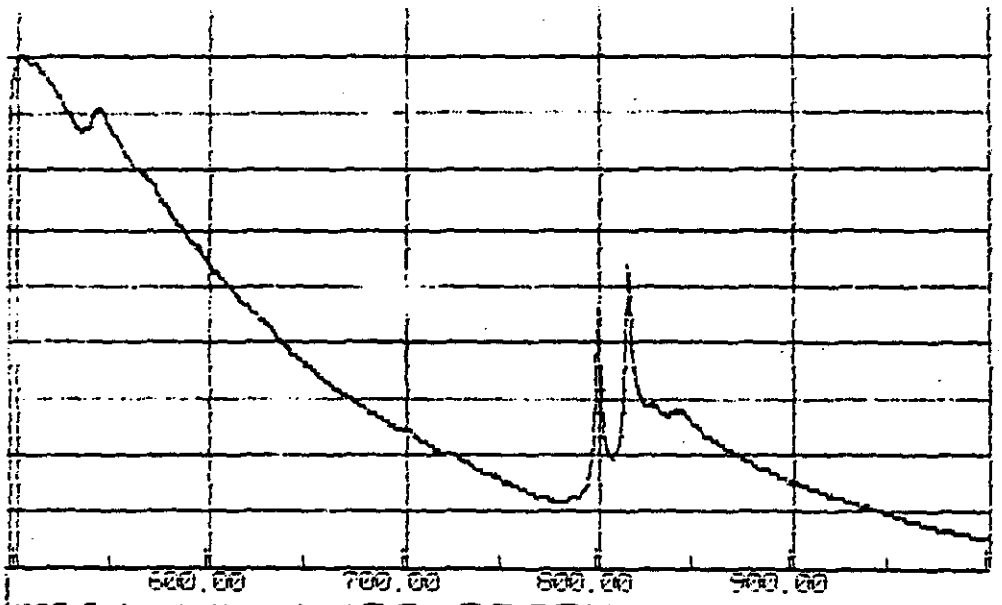
SCAN 1 OF 10DWELL: 5.000 SEC
OFFSET= 496.21EV/CH= 0.5188
LBL:
FS: 3516 MEM: A CNT: 2904



MODE:Refresh/Normal 496.206EV EDAX

No. 3

New Progress

With refer ce to the above experimental results and m nanism of radiation damage of BaF_2 crystals, ficient measures were made on raw materiai rocessing and crystal growth technology, w n have given new progress on the quality of large aF_2 crystal.

Fig.11 shc transmission curves of several newly grown c als after 1 MRad ^{60}Co irradiation.

Fig.12 sho that the radiation hardness of newly grown c tal is better than that of the best crystal grown b ore with the same length.

Fig.13 shov the experimental result of optical annealing of ne y grown crystal.

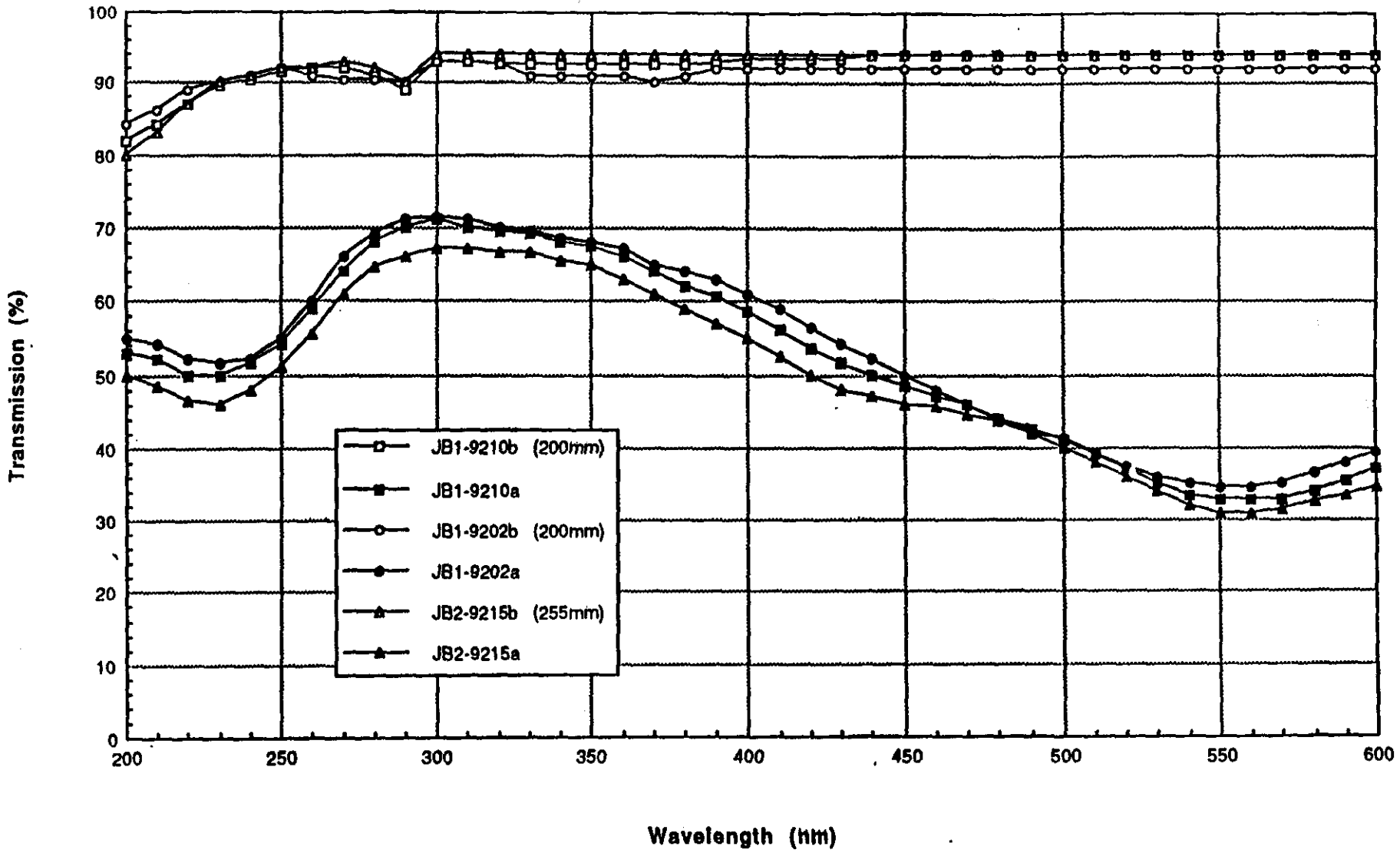


Fig.11 Transmission spectra of several new grown crystals before and after 1 MRad 60Co irradiation

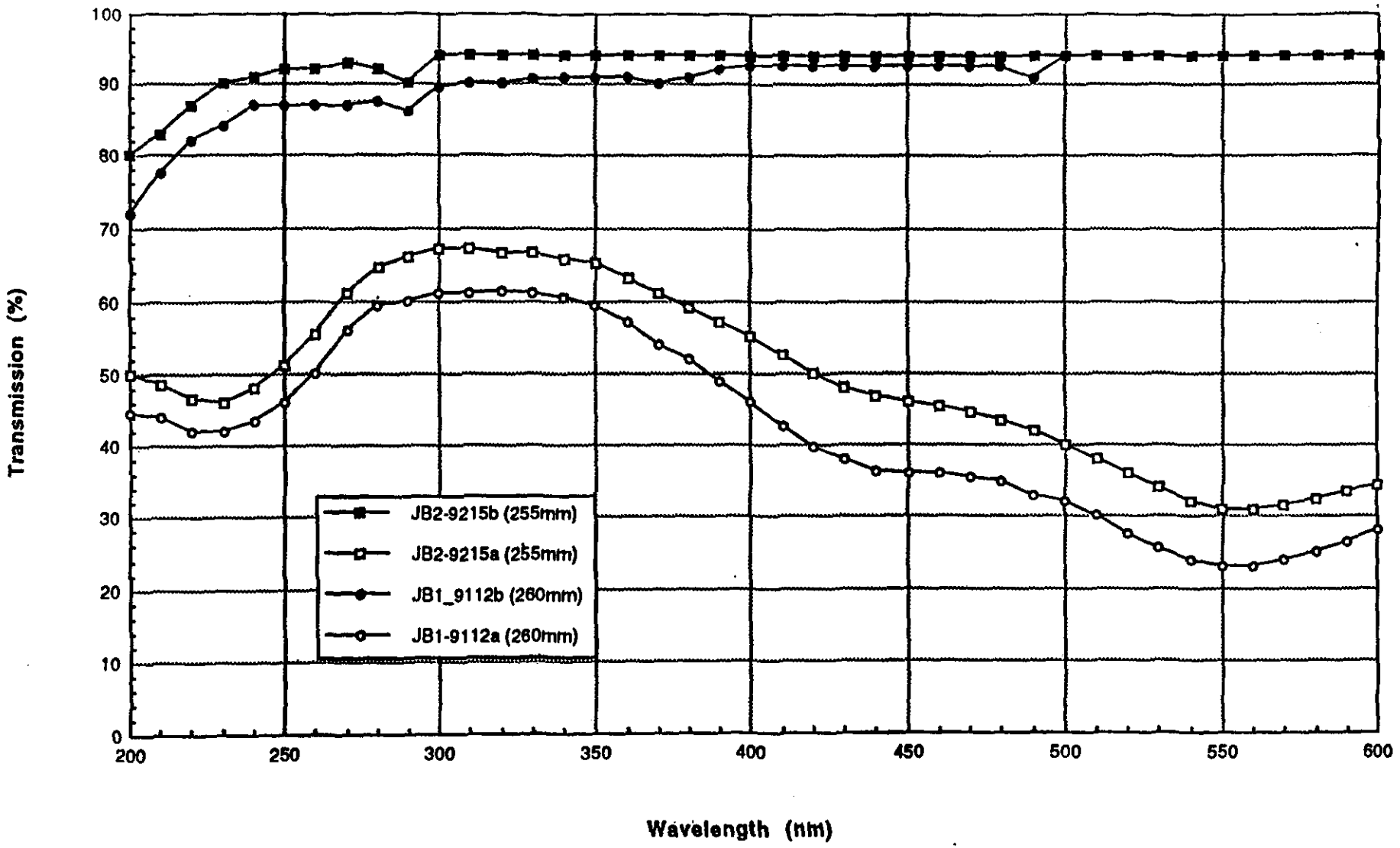


Fig. 12 Radiation hardness of new grown crystal compared with that of the best crystal grown before

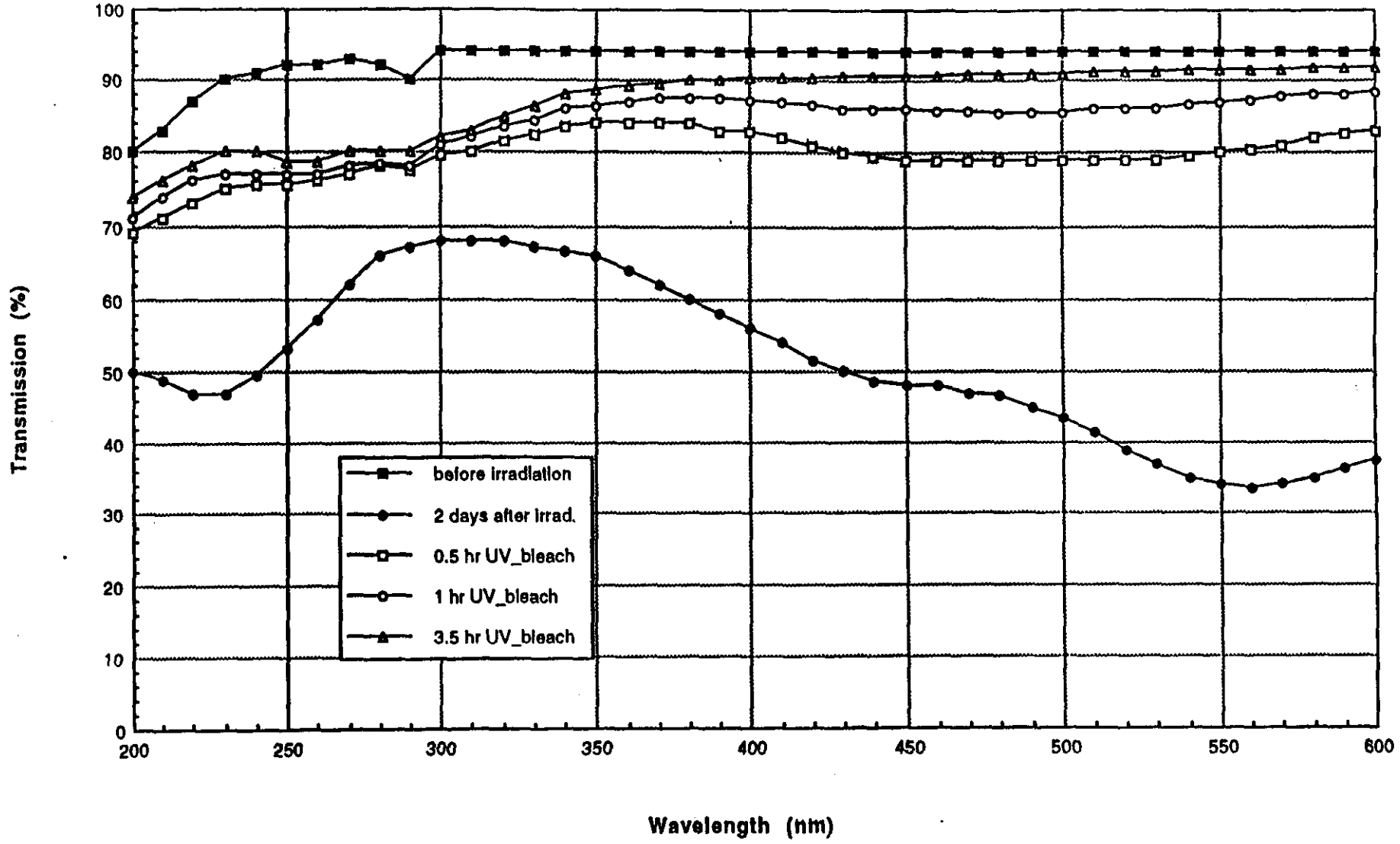


Fig.13 Experimental result of optical annealing of new grown crystal (UV_bleach with 80W high voltage Hg lamp)

Work to be Done in the Next Step

- Do comparative experiments on crystal growth with and without adopting the cool trap — to study its effect on radiation hardness.

- Ameliorate crystal growth and annealing techniques to produce crystals with less defects and more perfect structure, so that the radiation hardness can be improved.

- Design and build a new vacuum furnace with performance better than existing ones.

- Test for drying raw materials with gas flow.

- Continue to study the mechanism of radiation damage and impurity effect on it.

  -- Spectroscopy and Paramagnetic Resonance studies

  -- Electron Diffraction study

  -- Electron Energy Loss Spectrum (EELS) study

Materials
Characterization
BaF_2

Aug 31, 1992

Michael D. Strathman
Charles Evans & Assoc.

Trace Element Analysis

T Series ← High Rad Damage

+

S Series ← Low Rad Damage

Both Low in trace

T- 11,000 ppmw Sr

S- 240 ppm Sr

Table 6. GDMS analysis results of 1 Barium Fluoride sample.
S 52 # 14.
Analyzed by W.A. Vieth 8/25/92

Element		Concentration (ppm except as noted)		Element		Concentration (ppm except as noted)	
Li	<	0.15		Pd	<	9.1	
Be	<	0.0024		Ag	<	55	%
B	<	0.056		Cd	<	6.8	
C	<	220		In	<	0.011	
N	<	330		Sn	<	0.36	
O	<	0.19	%	Sb	<	33	
Na	<	0.27		Te	<	84	
Mg	<	0.082		I	<	43	
Al	<	0.43		Cs	<	0.61	
Si	<	1.9		BaF_2		100	%
P	<	0.24		La	<	2.9	
S	<	34		Ce	<	0.011	
Cl	~	120		Pr	<	0.037	
K	<	0.77		Nd	<	0.11	
Ca	<	5.3		Sm	<	1.8	
Sc	<	0.0010		Eu	<	280	
Ti	<	0.041		Gd	<	0.084	
V	<	0.0046		Tb	<	0.0066	
Cr	<	0.026		Dy	<	0.0083	
Mn	<	0.0031		Ho	<	0.0093	
Fe	<	0.18		Er	<	0.0054	
Co	<	0.0079		Tm	<	0.038	
Ni	<	0.011		Yb	<	0.037	
Cu	≤	0.58		Lu	<	0.015	
Zn	<	0.32		Hf	<	0.0099	
Ga	<	0.023		Ta	<	24	
Ge	<	0.014		W	<	0.096	
As	<	0.22		Re	<	0.020	
Se	<	0.44		Os	<	0.0095	
Br	<	0.14		Ir	<	0.0081	
Rb	<	0.10		Pt	<	0.021	
Sr		270		Au	<	0.077	
Y	<	1.1		Hg	<	0.069	
Zr	<	0.0058		Tl	<	0.13	
Nb	<	3.4		Pb	<	0.082	
Mo	<	0.040		Bi	<	0.0087	
Ru	<	0.016		Th	<	0.0014	
Rh	<	2.6		U	<	0.0053	

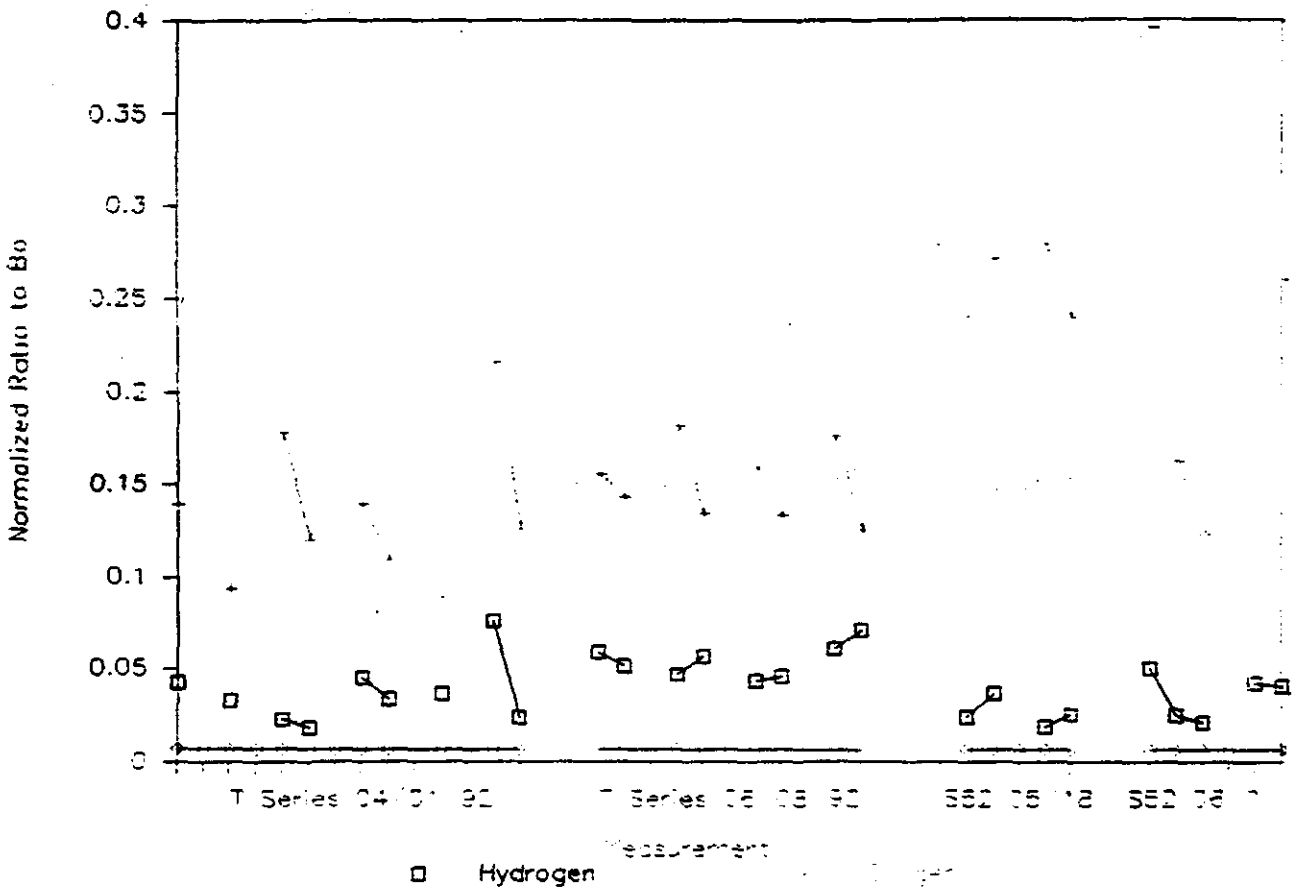
Notes:
C, N, O - well-known source contaminants
Ag - conducting binder
Ta - source material
F, Ba - matrix elements
Na, Al, S, Fe, As, Mo, Sn, W - impurities detected in Ag powder
Rh, Pd, Cd, Sb, I, Te, Cs, La, Sm, Eu - unresolved from interfering signals.
Si - mortar material.
Li, Nb - memory.

Table 1. GDMS analysis results of 1 Barium Fluoride sample.
T 1.
Analyzed by W.A. Vieth 8/24/92

Element		Concentration (ppm except as noted)		Element		Concentration (ppm except as noted)	
Li	<	1.		Rh	<	72	
Be	<	0.0059		Ag	<	68	%
B		0.19		Cd	<	2.0	
C	<	250		In	<	0.016	
N	<	260		Sn	<	0.23	
O	<	1700		Sb	<	26	
Na		1.		Te	<	17	
Mg		0.32		I	<	2.3	
Al		8.		Cs	<	0.44	
Si	≤	6.1		BaF_2		100	%
P	<	0.3		La	<	2.8	
S	~	82		Ce	<	0.025	
Cl	~	140		Pr	<	0.069	
K	<	1.		Nd	<	0.14	
Ca	~	20		Sm	<	1.9	
Sc	<	0.0016		Eu	<	250	
Ti	<	0.17		Gd	<	0.13	
V	<	0.0017		Tb	<	0.014	
Cr	<	0.079		Dy	<	0.019	
Mn	<	0.0044		Ho	<	0.016	
Fe	<	0.27		Er	<	0.0084	
Co	<	0.0052		Tm	<	0.0063	
Ni	<	0.021		Yb	<	0.030	
Cu	<	0.29		Lu	<	0.023	
Zn	<	0.15		Hf	<	0.032	
Ga	<	0.039		Ta	<	31	
Ge	<	0.066		W	<	0.36	
As	<	0.15		Re	<	0.033	
Se	<	0.47		Os	<	0.016	
Br	<	0.22		Ir	<	0.015	
Rb	<	0.069		Pt	<	0.083	
Sr		11000		Au	<	0.22	
Y	<	1.0		Hg	<	0.17	
Zr	<	0.0090		Tl	<	0.21	
Nb	<	3		Pb	<	0.028	
Mo	<	0.038		Bi	<	0.018	
Ru	<	0.030		Th	<	0.0027	
Pd	<	50		U	<	0.010	

Notes:
C, N, O - well-known source contaminants
Ag - conducting binder
Ta - source material
F, Ba - matrix elements
Na, Al, S, Fe, As, Mo, Sn, W - impurities detected in Ag powder
Rh, Pd, Cd, Sb, I, Te, Cs, La, Sm, Eu - unresolved from interfering signals.
Si - mortar material.
Li, Nb - memory.

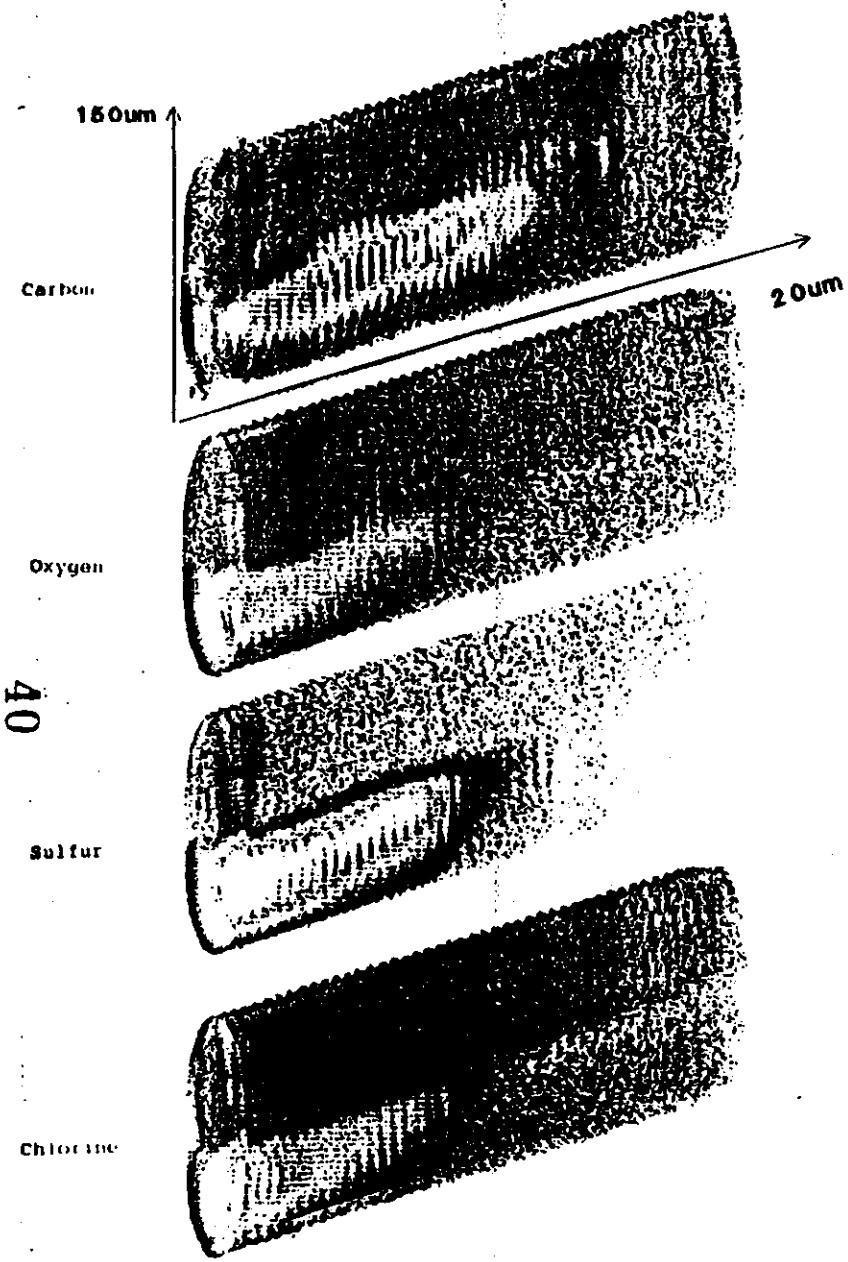
SIMS Bulk Analysis



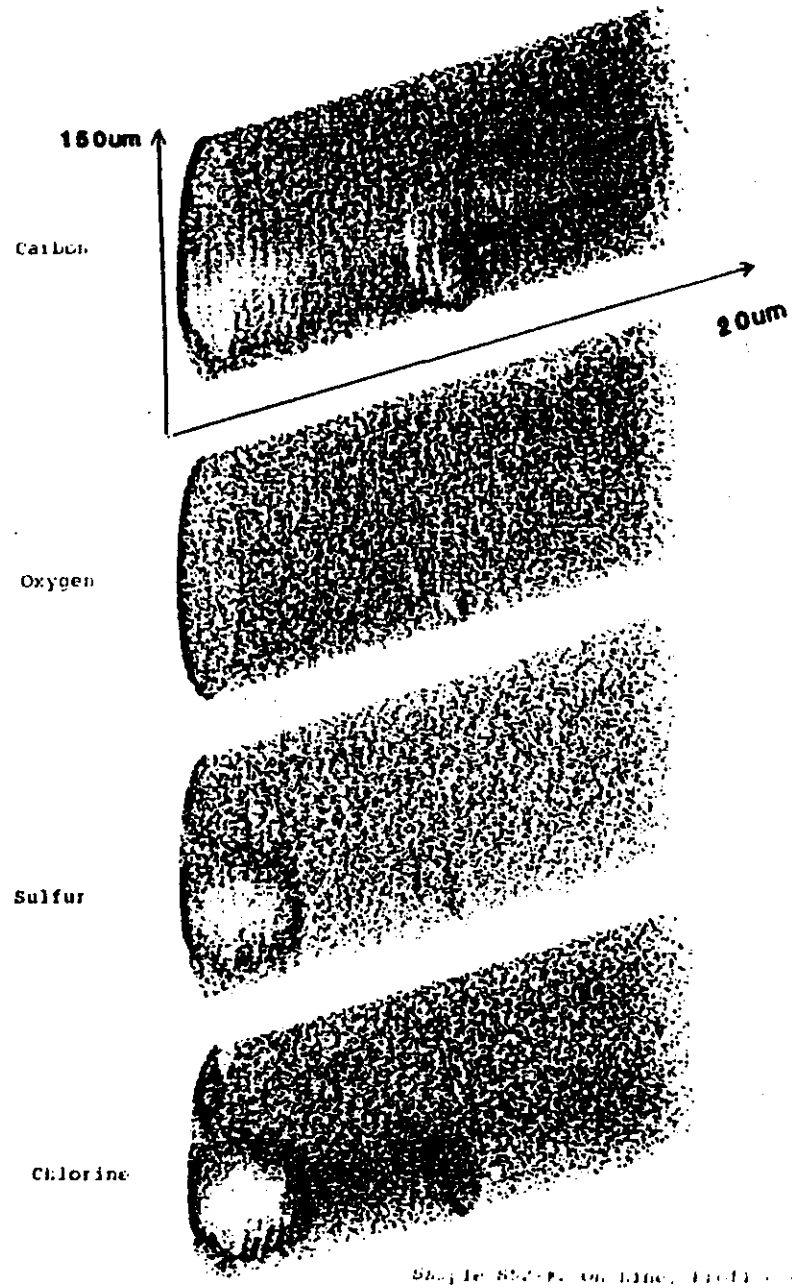
Normalized SIMS Yields

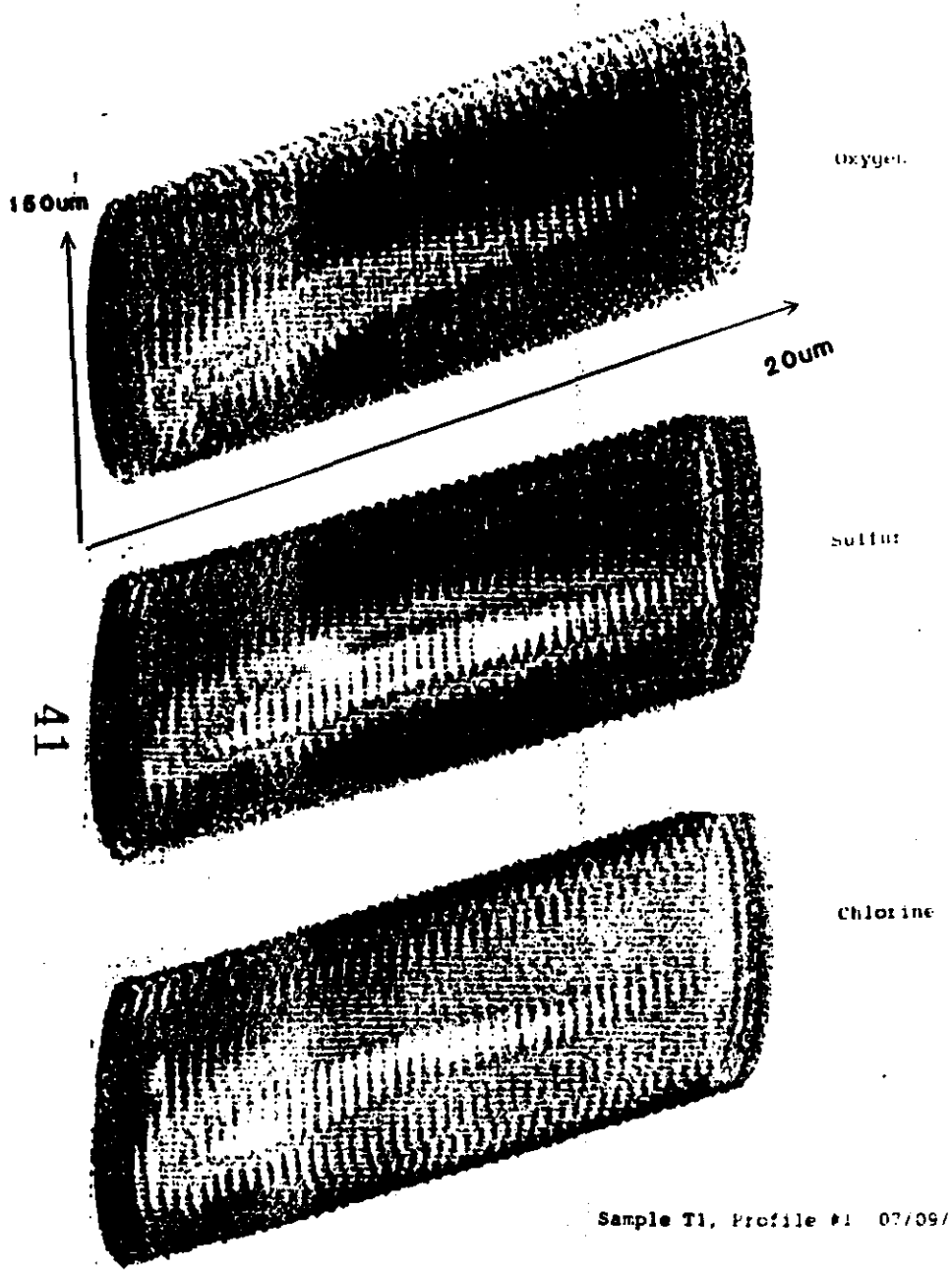
		H	O
T Series:			
April 1, 1992	**AVG**	**0.037**	**0.134**
	STD	**0.016**	**0.038**
June 8, 1992	**AVG**	**0.056**	**0.151**
	STD	**0.009**	**0.019**
	Leco AVG (ppm)		**52.346**
	STD		**15.392**
S52 Series:			
May 18, 1992	**AVG**	**0.031**	**0.244**
	STD	**0.011**	**0.088**
June 1, 1992	AVG	0.036	0.228
	STD	0.011	0.095
	Leco AVG (ppm)		44.500
	STD		9.309

Figure #2

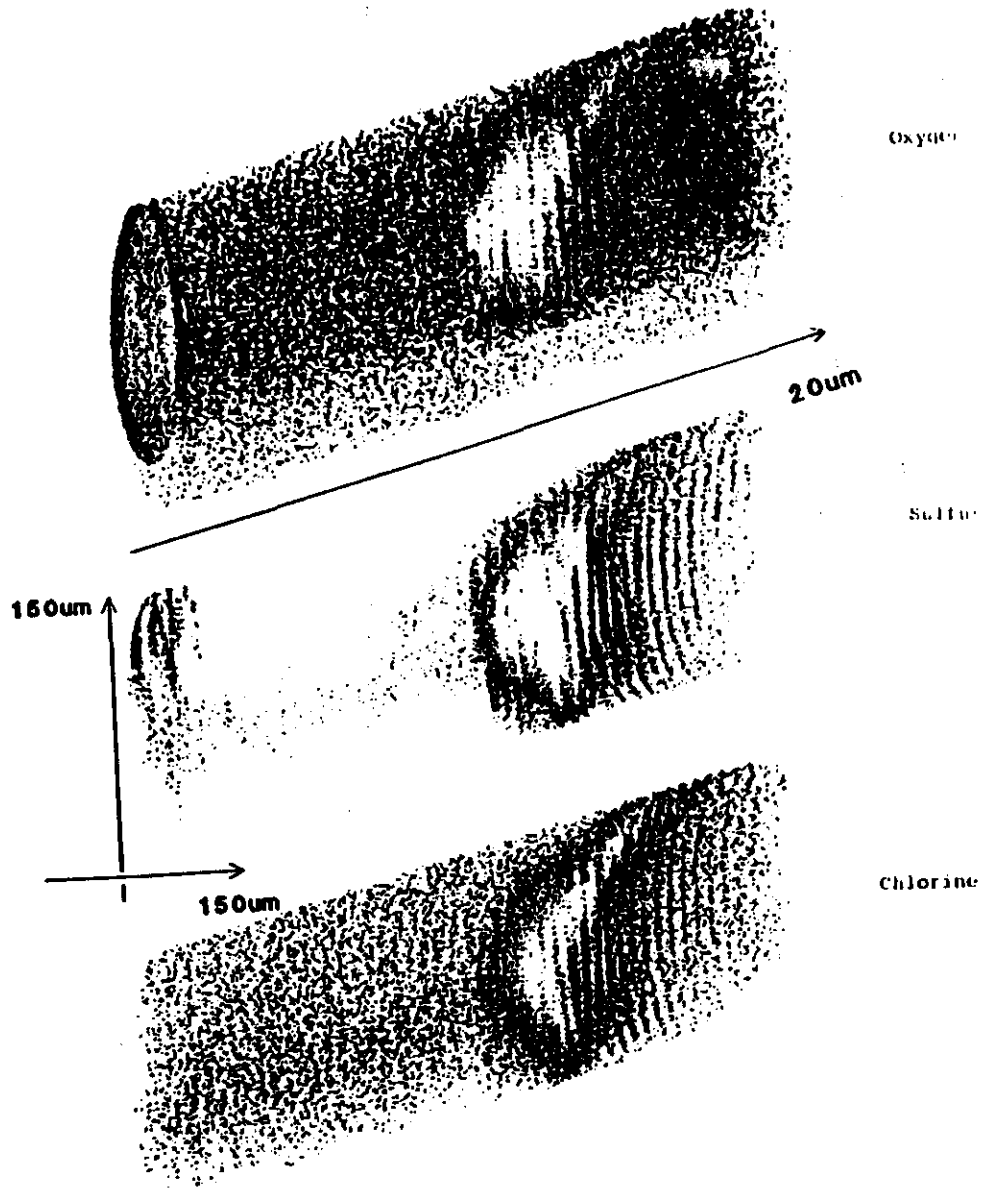


Sample T1, Line through Sample Profile





Sample T1, Profile #1 07/09/9



Sample S52-

RBS / Lateral Channeled Scan

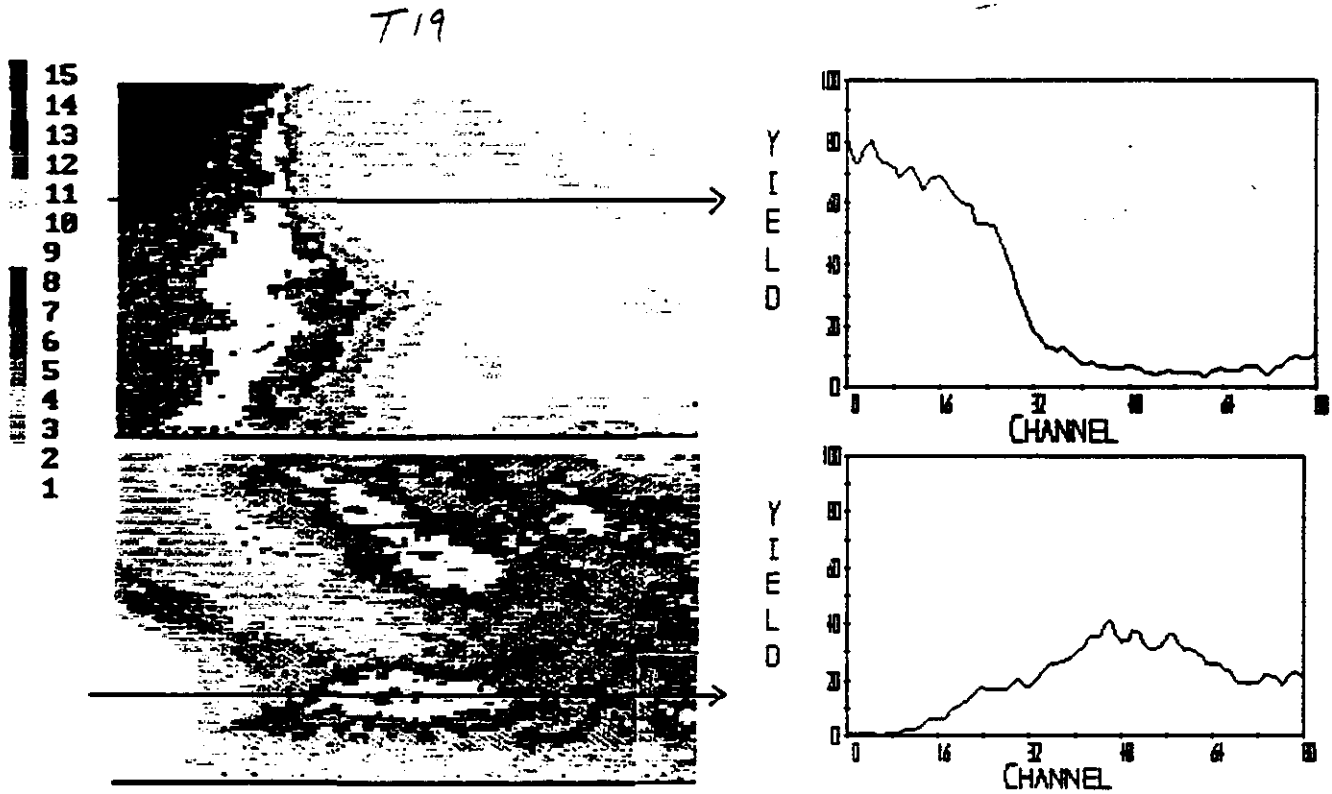


Fig #1

Comparison

of

Air & N_2

Anneal

1) SEM

2) Channelling

K144304 A.1

K144304 A.1

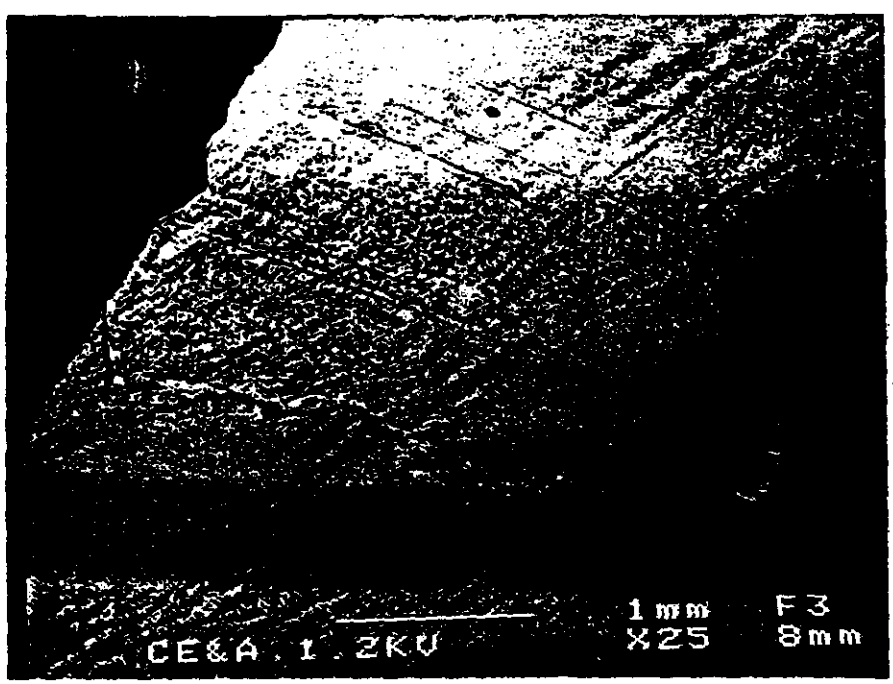


Fig 1

K14430A A.i

K14430A A.i

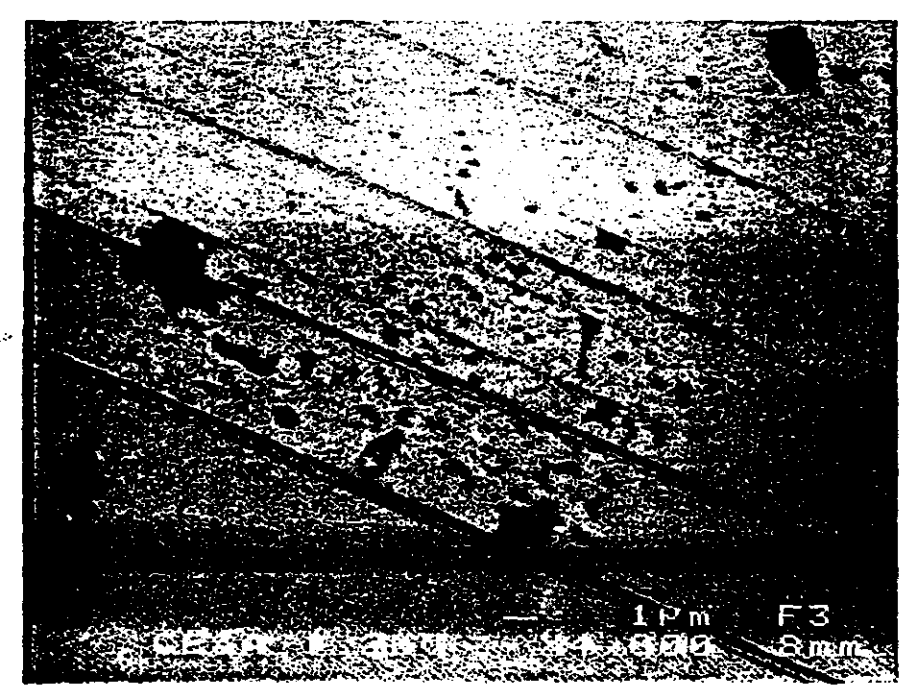
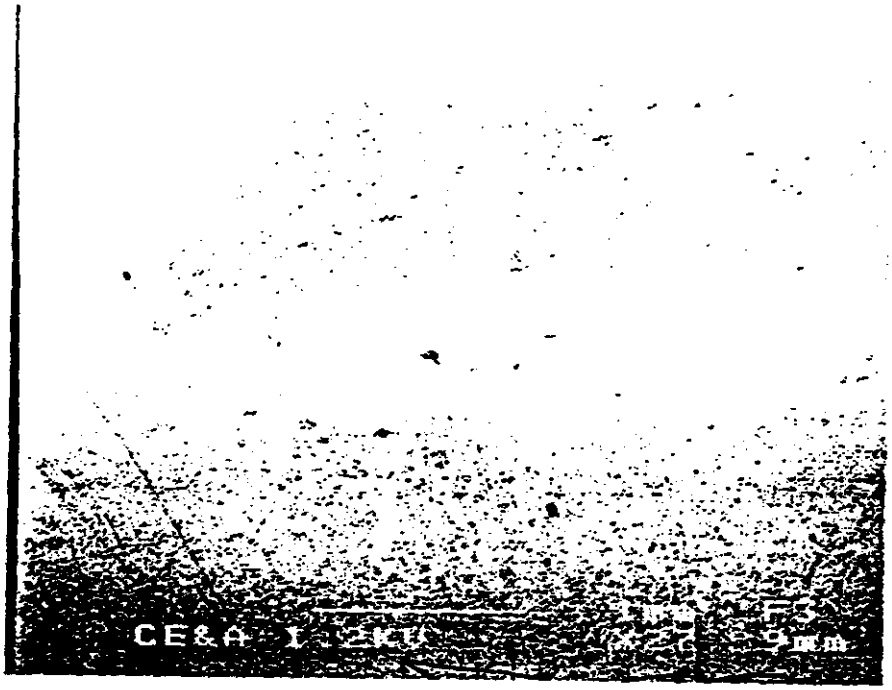


Fig #2



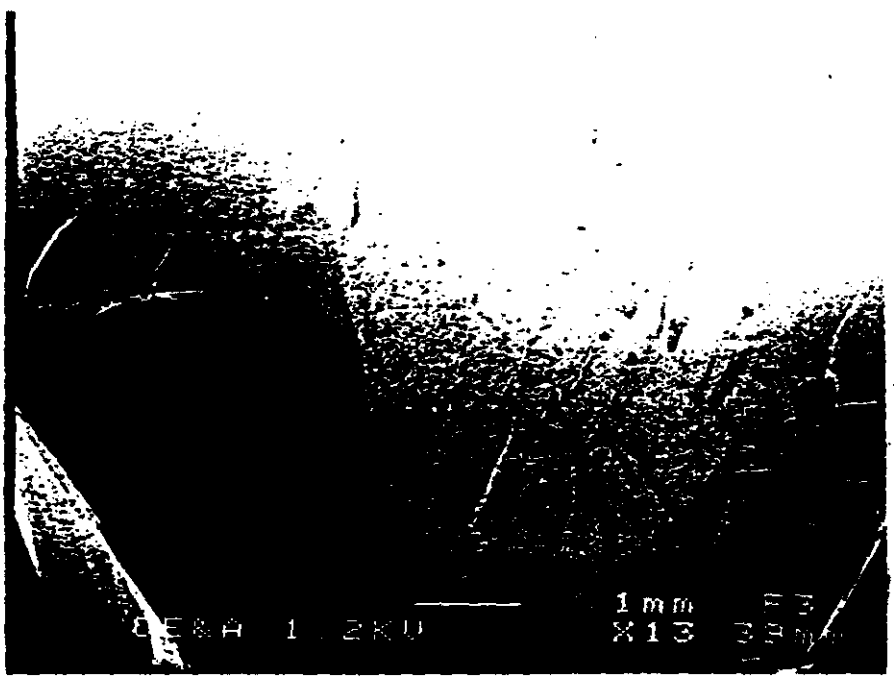
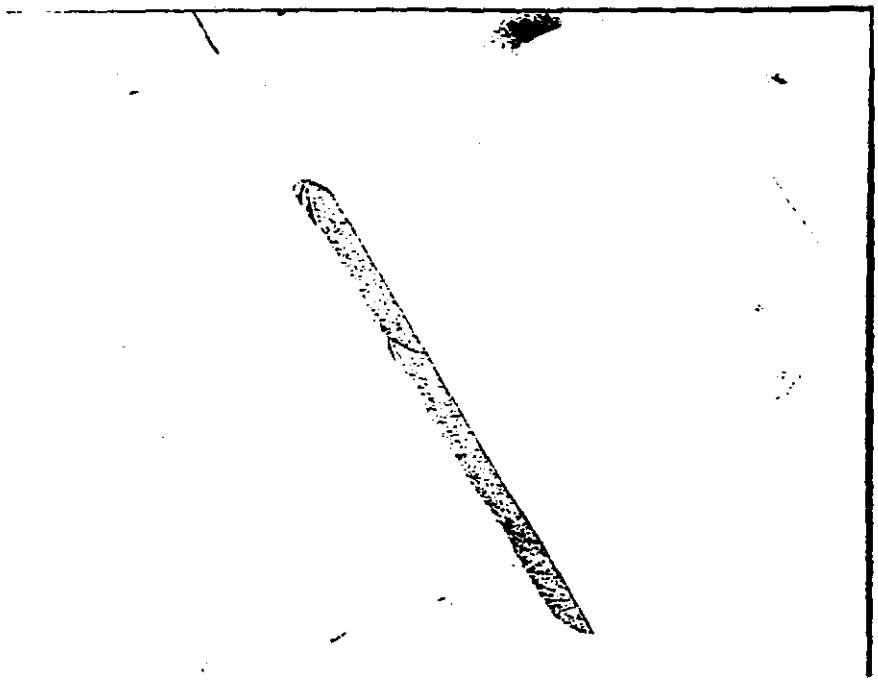
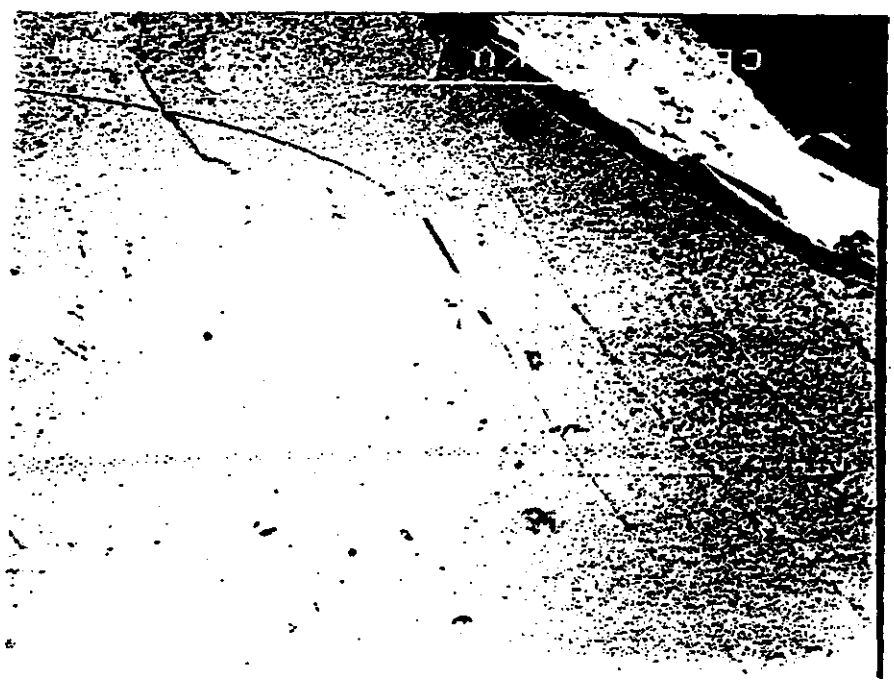


Fig #3



K14417B N_2



K14417B N_2

Channeled Lattera/ RBS Scan

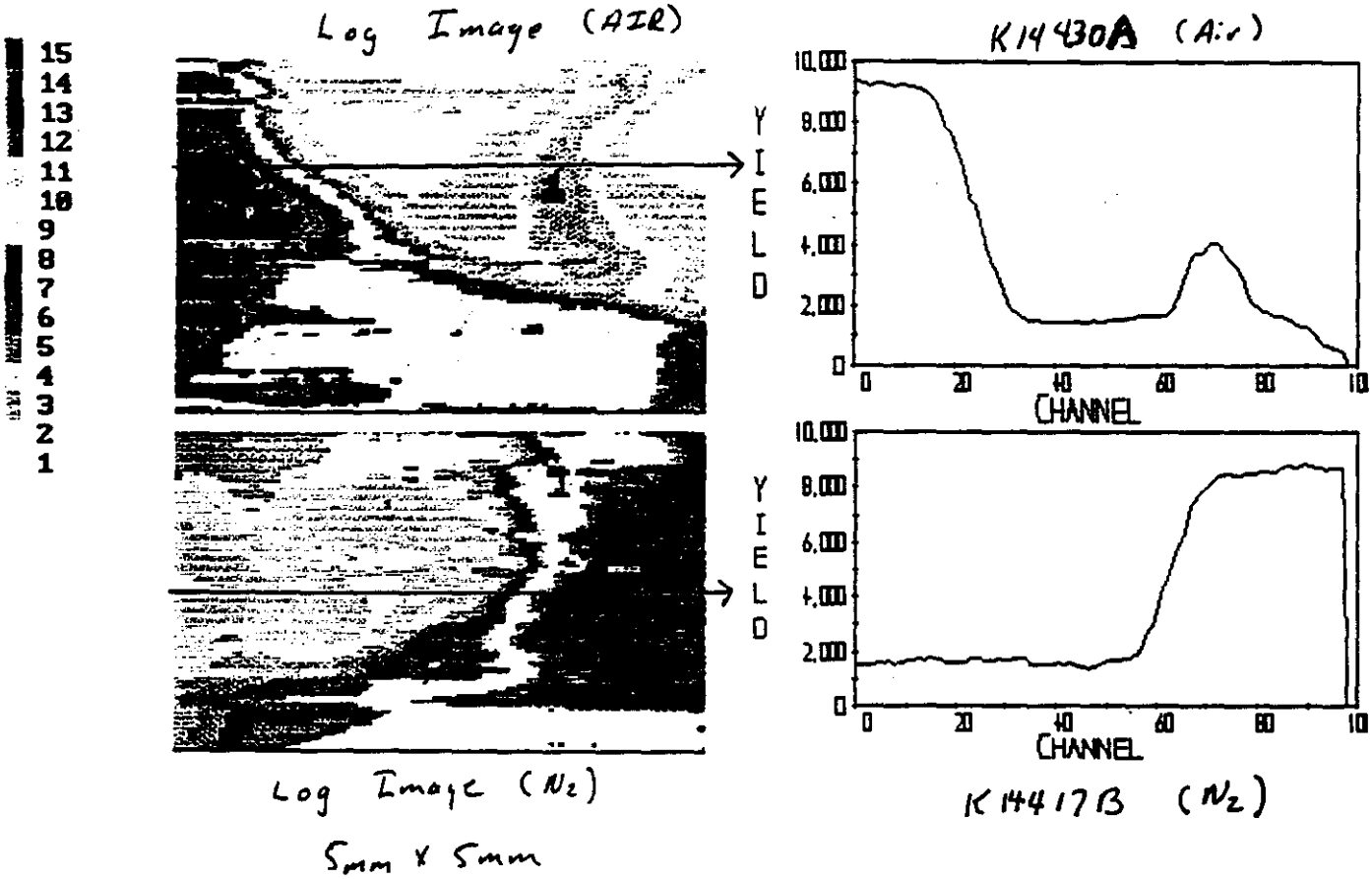
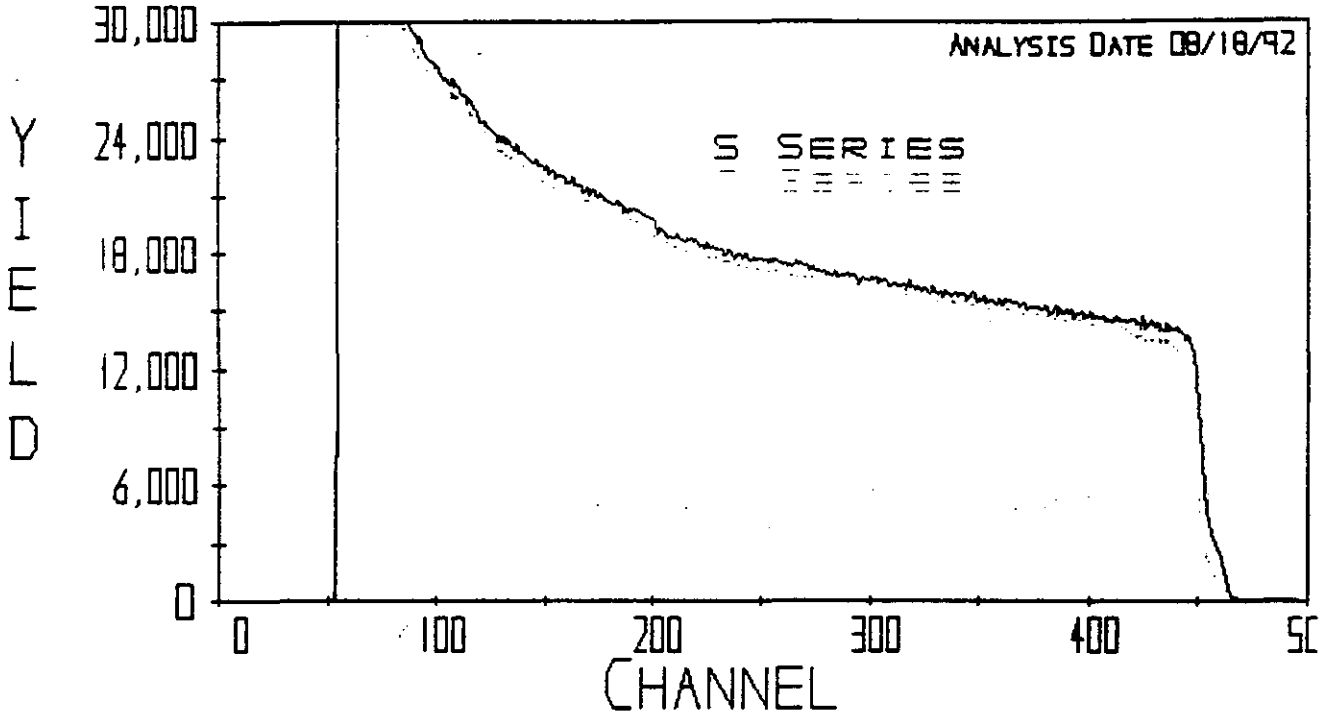


Fig #1

RBS of BaF2



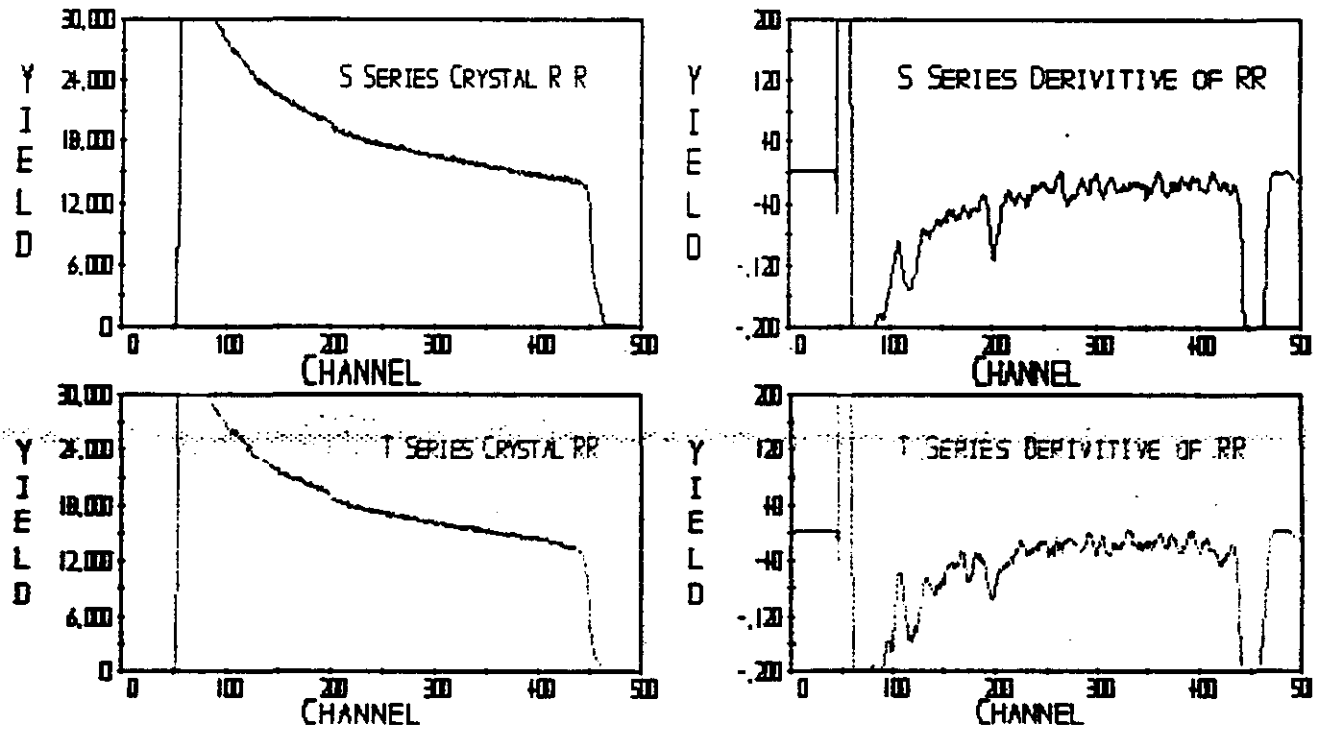
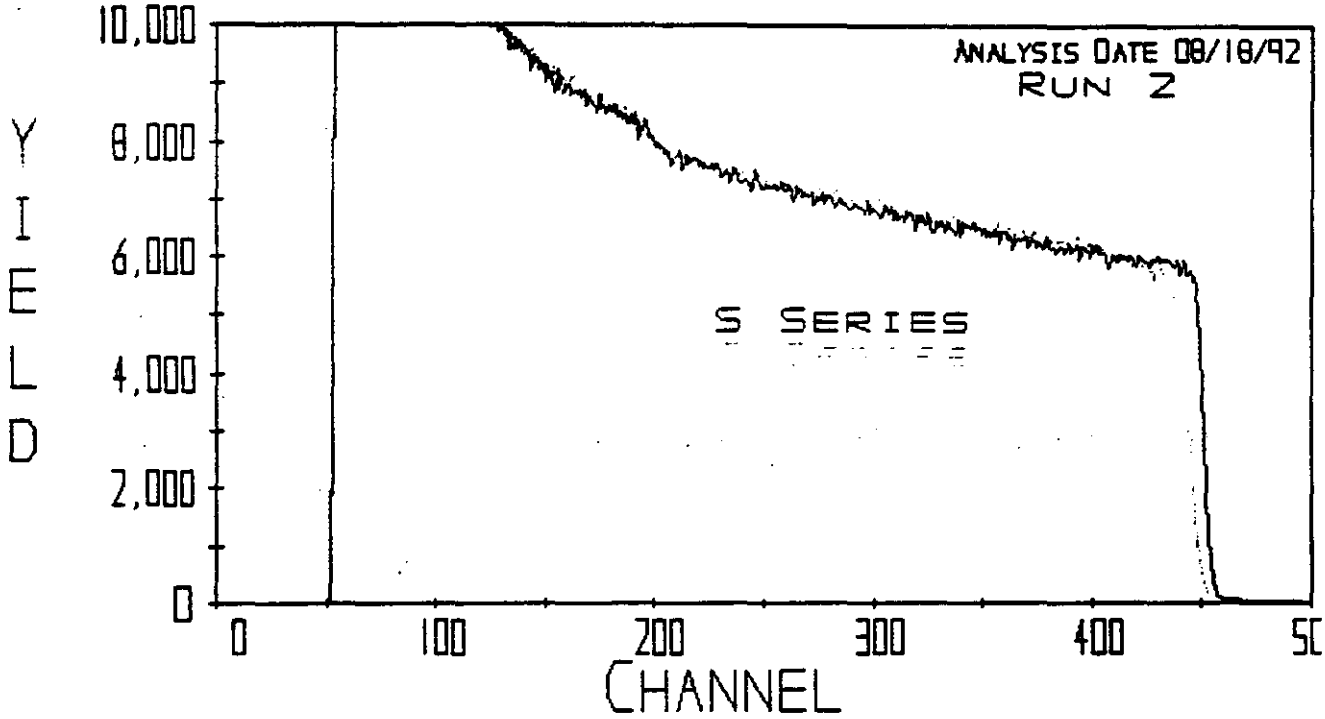


Fig #2

RBS of BaF2



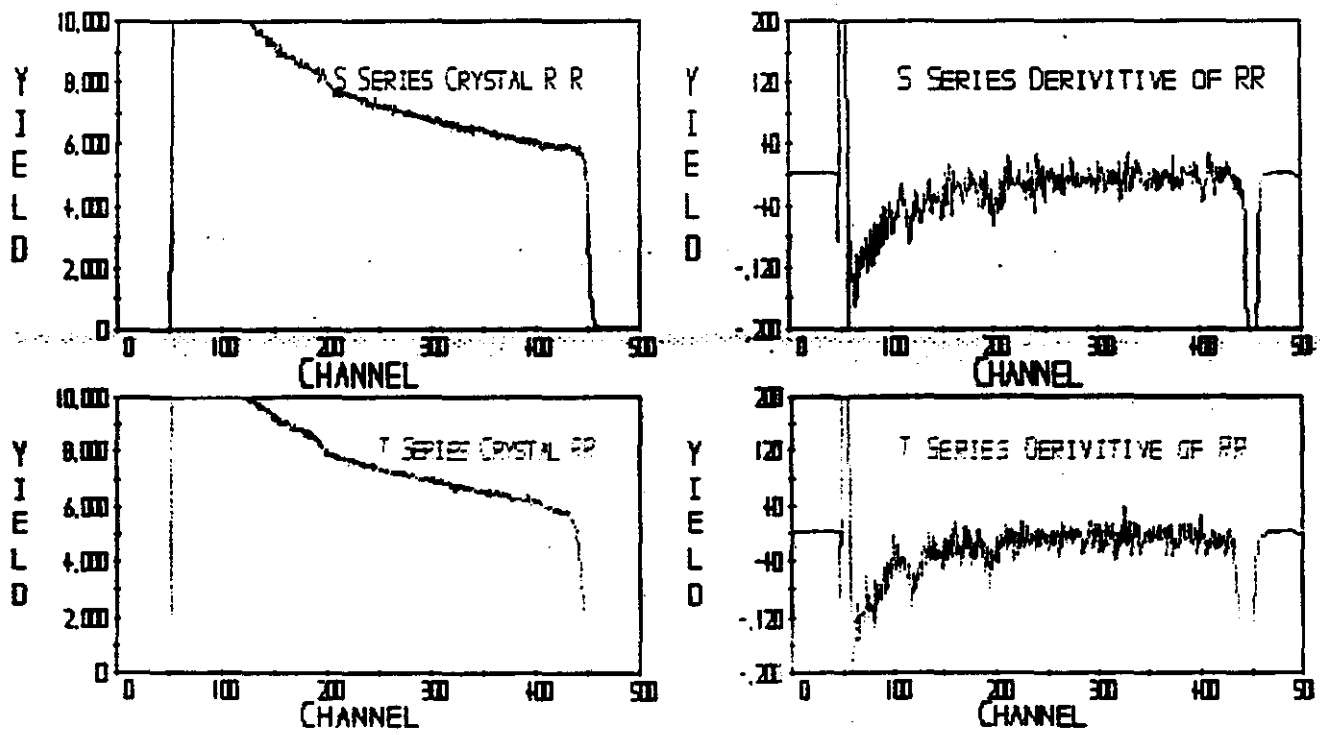


Fig #3

FLUORIKAIN (BDH)

infrared glass material

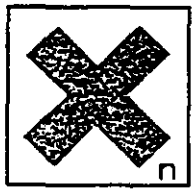
BARIUM FLUORIDE Fibre Grade — **Product Number 58155**

BaF_2	MW	175.34
	SG	4.89
	Mp	1368°C
	Bp	2272°C

Melt grown; crystal fragments.

Mass-Spectrographic Analysis

Uranium	U	< .01
Thorium	Th	< .01
Bismuth	Bi	< .01
Lead	Pb	< .02
Thallium	Tl	< .01
Mercury	Hg	< .03
Gold	Au	< .03
Platinum	Pt	< .03
Iridium	Ir	< .02
Osmium	Os	< .02
Rhenium	Re	< .02
Tungsten	W	< .1
Tantalum	Ta	< .1
Hafnium	Hf	< .1
Lutetium	Lu	< .1
Ytterbium	Yb	< .4
Thulium	Tm	< .01
Erbium	Er	< .03
Holmium	Ho	< .01
Dysprosium	Dy	< .4
Terbium	Tb	< .1
Gadolinium	Gd	-
Europium	Eu	< .6
Samarium	Sm	< .04
Neodymium	Nd	< .04
Praseodymium	Pr	< .1
Cerium	Ce	< .1
Lanthanum	La	< 1
Barium	Ba	Base
Caesium	Cs	< .01
Iodine	I	< .01
Tellurium	Te	< .3
Antimony	Sb	< .06
Tin	Sn	< .1
Indium	In	< .01
Cadmium	Cd	< .03
Silver	Ag	< .02
Palladium	Pd	< .05
Rhodium	Rh	< .01
Ruthenium	Ru	< .02
Molybdenum	Mo	< .03
Niobium	Nb	< .01
Zirconium	Zr	3
Yttrium	Y	< .1
Strontium	Sr	30
Rubidium	Rb	< .01
Bromine	Br	0.6
Selenium	Se	< .02
Arsenic	As	.3
Germanium	Ge	< .03
Gallium	Ga	< .03
Zinc	Zn	.02
Copper	Cu	.01
Nickel	Ni	< .03
Cobalt	Co	< .1
Iron	Fe	.3
Manganese	Mn	< 0.01
Chromium	Cr	< .01
Vanadium	V	< .01
Titanium	Ti	< .01
Scandium	Sc	< 1
Calcium	Ca	10
Potassium	K	.3
Chlorine	Cl	3
Sulphur	S	3
Phosphorus	P	1
Silicon	Si	3
Aluminium	Al	1
Magnesium	Mg	< .01
Sodium	Na	< .01
Fluorine	F	Base
Oxygen	O	-
Nitrogen	N	-
Carbon	C	-
Boron	B	.03
Beryllium	Be	< .01
Lithium	Li	< .01



Harmful

All figures are quoted in ppm atomic

Harmful by inhalation and if swallowed.
Avoid contact with skin and eyes.

The sale of materials described in this data sheet will be covered by the General Conditions of Sale of BDH Limited, a copy of which is available on request.

BDH Limited, Broom Road, Poole, BH12 4NN, England. Telephone: National (0202) 745520 International +44 202 745520 Telex: 41186 and 418123 TETRA G. Cables: Tetradome Poole. Fax Group III: (0202) 738299

June 1993

Table 2 GDMS analysis of BaF_2 (Chinese Powder) F.L. 8/5/92

Element		Concentration (ppm except as noted)	Element		Concentration (ppm except as noted)
Li	<	0.00062	Pd	<	2.0
Be	<	0.0011	Ag		120
B		0.078	Cd	≤	0.90
C	<	130	In		0.23
N	<	1600	Sn	≤	0.74
O	<	1800	Sb	<	67
Na	~	4.	Te	<	140
Mg		0.70	I	<	9.8
Al		2.0	Cs	<	0.62
Si	~	33	La	<	11
P		0.67	Ce	<	0.007
S	~	50.	Pr	<	0.10
Cl	~	78	Nd	<	0.015
K	<	0.55	Nd	<	0.085
Ca	<	0.68	Sm	<	12
Sc		0.020	Eu	<	280
Ti	<	0.11	Gd	<	0.063
V		0.0039	Tb	<	0.0074
Cr		0.2	Dy	<	0.054
Mn		0.027	Ho	<	0.0024
Fe	<	0.92	Er	<	0.0070
Co	<	0.014	Tm	<	0.0032
Ni	<	0.11	Yb	<	0.041
Cu		0.2	Lu	<	0.0046
Zn	<	0.17	Hf	<	0.016
Ga		0.15	Ta	<	15
Ge	<	0.15	W	<	0.082
As	<	1.1	Re	<	0.0090
Se		360	Os	<	0.0023
Br	≤	0.62	Ir	<	0.0023
Rb	<	0.088	Pt	<	0.084
Sr		71	Au	<	0.12
Y	<	0.22	Hg	≤	0.46
Zr	<	0.026	Tl	<	0.041
Nb	<	0.028	Pb		1400
Mo	<	4.	Bi	≤	0.026
Ru	<	0.093	Th	<	0.00035
Rh	<	0.60	U	<	0.0030

Notes:
C, N, O – well-known source contaminants
Ag – conducting binder
Ta – source material
F, Ba – matrix elements
Na, Al, S, Fe, As, Mo, Sn, W – impurities detected in Ag powder
Rh, Pd, Cd, Sb, I, Te, Cs, La, Sm, Eu – unresolved from interfering signals.
Si – mortar material.

Table 1 GDMS analysis of BaF_2 (Chinese Crystal) F.L. 8/5/9

Element		Concentration (ppm except as noted)	
Li	<	0.00095	
Be	<	0.0043	
B		0.15	
C	<	0.019	%
N	<	0.13	%
O	<	0.25	%
Na		38	
Mg		2.6	
Al		16.	
Si	~	58	
P		0.68	
S	~	40.	
Cl	~	72	
K	<	1.2	
Ca		13	
Sc	<	0.018	
Ti	<	0.17	
V		0.017	
Cr	<	0.096	
Mn		0.088	
Fe	≤	0.8	
Co	<	0.021	
Ni	<	0.10	
Cu		1.0	
Zn	<	0.46	
Ge	<	0.070	
Ga		0.082	
As	<	1.0	
Se		7.5	
Br	<	0.074	
Rb	<	0.085	
Sr		420	
Y	<	0.76	
Zr	<	0.0060	
Nb	<	0.028	
Mo	<	2.	
Ru	<	0.0046	
Rh	<	8.3	

Element		Concentration (ppm except as noted)	
Pd	<	0.59	
Ag		110	%
Cd	≤	0.87	
In		0.079	
Sn	≤	1.8	
Sb	<	51	
Te	<	65	
I	<	34	
Cs	<	0.22	
La	<	5.2	
Ce	<	0.093	
Pr	<	0.088	
Nd	<	0.48	
Sm	<	68	
Eu	<	1200	
Gd	<	0.15	
Tb	<	0.020	
Dy	<	0.068	
Ho	<	0.011	
Er	<	0.033	
Tm	<	0.0061	
Yb	<	0.19	
Lu	<	0.24	
Hf	<	0.017	
Ta	<	13	
W	<	0.095	
Re	<	0.011	
Os	<	0.012	
Ir	<	0.015	
Pt	<	0.034	
Au	<	0.19	
Hg	≤	0.46	
Tl	<	0.041	
Pb		1.3	
Bi	<	0.0071	
Th	<	0.0024	
U	<	0.0028	

Notes:
C, N, O - well-known source contaminants
Ag - conducting binder
Ta - source material
F, Ba - matrix elements
Na, Al, S, Fe, As, Mo, Sn, W - impurities detected in Ag powder
Rh, Pd, Cd, Sb, I, Te, Cs, La, Sm, Eu - unresolved from interfer
Si - mortar material. signa

(Fax 510-423-8086)

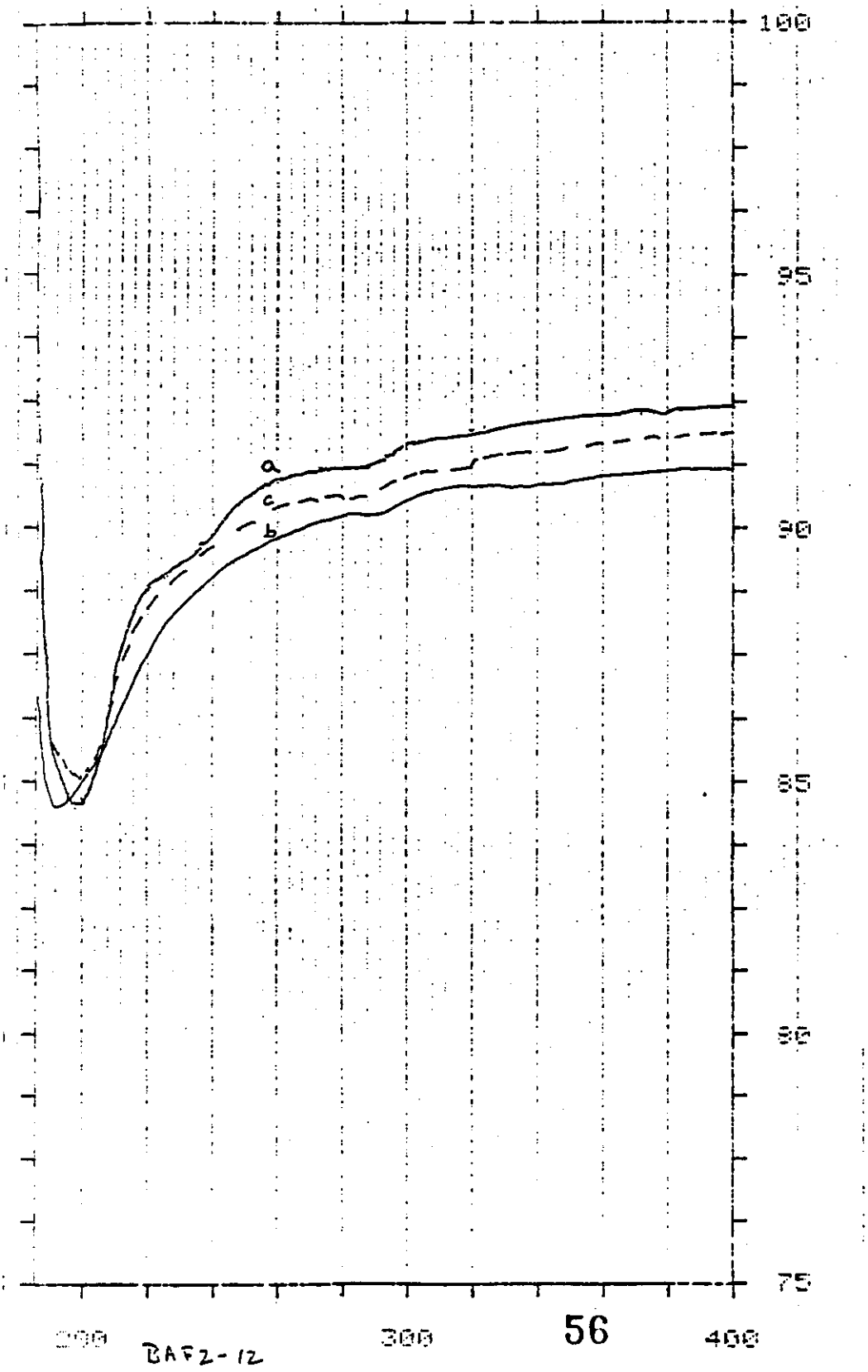
Table 3 GDMS analysis of BaF_2 (BDH-651232/001) F.L. 8/5/92

Element		Concentration (ppm except as noted)	Element		Concentration (ppm except as noted)
Li		0.038	Pd	<	0.58
Be	<	0.00088	Ag		120 %
B		0.081	Cd	<	1.2
C	<	76	In		0.39
N	<	2000	Sn	≤	0.54
O	<	2400	Sb	<	68
Na	~	4.	Te	<	230
Mg		1.3	I	<	18
Al		2.	Cs	<	1.1
Si	~	58	La	<	13
P		0.63	Ce	<	0.0076
S	~	47.	Pr	<	0.096
Cl	~	80	Nd	<	0.012
K	<	0.4	Sm	<	4.5
Ca	<	0.35	Eu	<	280
Sc	<	0.0018	Gd	<	0.055
Ti	<	0.26	Tb	<	0.0051
V		0.026	Dy	<	0.0066
Cr		0.2	Ho	<	0.0017
Mn		0.067	Er	<	0.0027
Fe	<	1.2	Tm	<	0.0020
Co	<	0.010	Yb	<	0.0079
Ni	<	0.11	Lu	<	0.0024
Cu	≤	0.1	Hf	<	0.0060
Zn	<	0.23	Ta	<	20
Ge	<	0.063	W	<	0.12
Ga		0.15	Re	<	0.0075
As	<	1.3	Os	<	0.0023
Br	<	0.12	Ir	<	0.0013
Se		200	Pt	<	0.031
Rb	<	0.091	Au	<	0.083
Sr		18	Hg	≤	0.43
Y	<	0.32	Tl	<	0.046
Zr	<	0.0040	Pb		1.5
Nb	<	0.017	Bi	<	0.013
Mo	<	1.	Th	<	0.00084
Ru	<	0.092	U	<	0.0018
Rh	<	0.36			

Notes:
C, N, O - well-known source contaminants
Ag - conducting binder
Ta - source material
F, Ba - matrix elements
Na, Al, S, Fe, As, Mo, Sn, W - impurities detected in Ag powder
Rh, Pd, Cd, Sb, I, Te, Cs, La, Sm, Eu - unresolved from interfering signals
Si - mortar material.

Figure 1

SAMPLE BAF2-12 , Exp series 2



a. Initial T

b. After ^{60}Co exposure

$2.9 \frac{krad}{hr} \times 29 \text{ hrs} = 84 \text{ krad}$

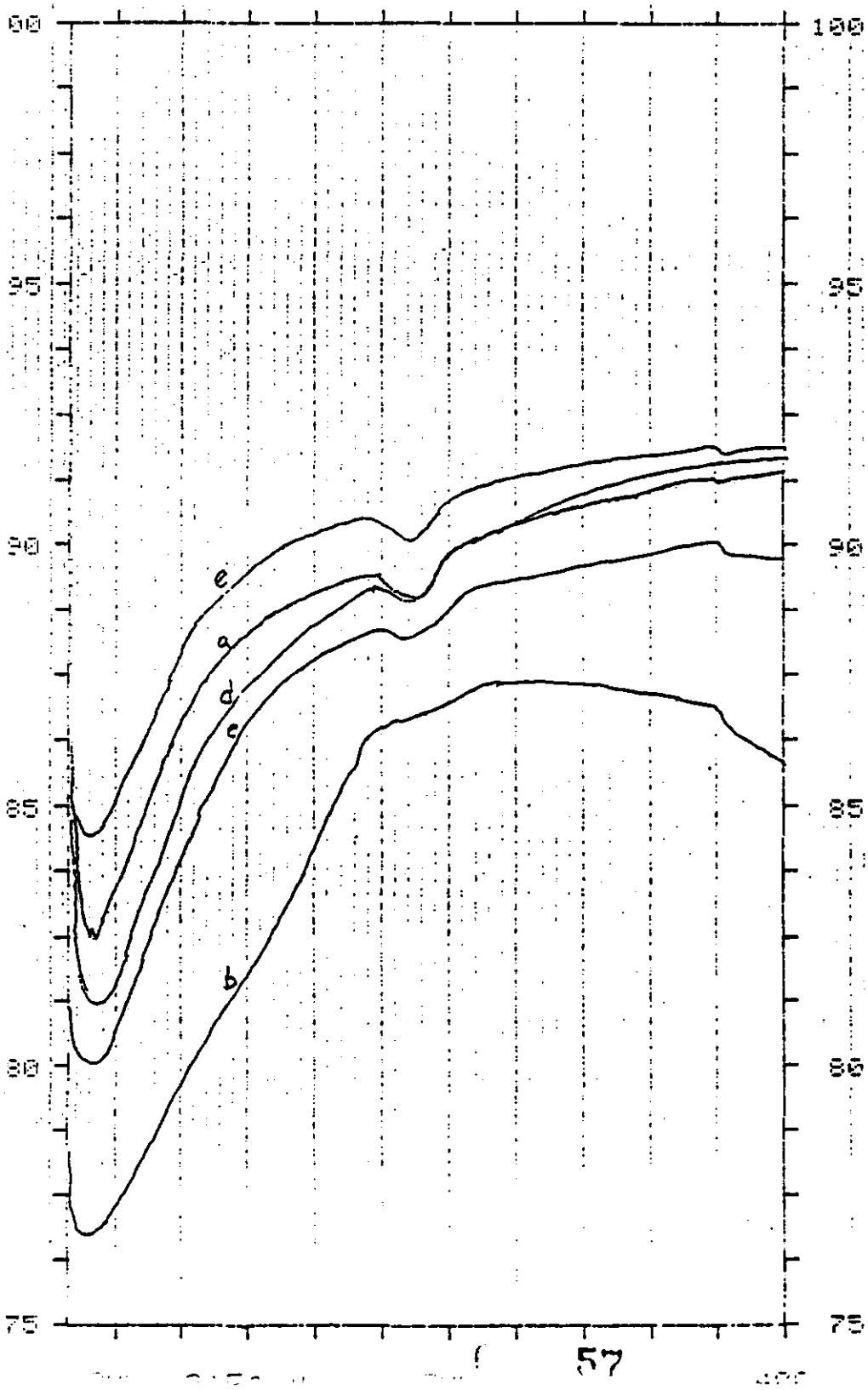
with UV illumination

254 nm @ .004 W/cm^2

c. After 4 days storage in dessicator w/ room lights.

Figure 2

Sample BAF2-11, Exp. series 2



a) Initial T

b) After ^{60}Co exposure
$2.9 \frac{krad}{hr} \times 29$ hrs.
$= 84$ krad.
(NO UV exposure)

c) 0.5 hr wt. light

d) 17 hrs white light illumination
20 watt tungsten bulb
1 m F.O. cable (silica)

e) 1.25 hrs UV
254 nm @ .004 W/cm^2

BaF_2 EM CALORIMETER REQUIREMENTS FOR 8/92 GEM DECISION:

DEMONSTRATE CAPABILITY TO MAINTAIN THE HIGH RESOLUTION IN SITU

RADIATION HARD CRYSTALS

(1) Demonstrate Substantial Improvement in 20 - 25 cm Crystals. $\lambda > 60$ cm After 1 MRad By 8/92.

(2) Produce Small Rad Hard Crystals: $\lambda \geq 95$ cm After 1 MRad. Show There are No Fundamental Limitations. (Recommended By Expert Panel).

LIGHT COLLECTION UNIFORMITY

(1) Develop Detailed Plan for Obtaining Uniform Crystals After Wrapping Or Coating.

(2) Demonstrate Stability, Or Specify Max. Non-Uniformity (and Time Dependence) Induced By Irradiation.

(3) Pre-Irradiation Question: Method; Time Dependence Due To Incomplete Saturation, or Annealing In Situ.

(4) Cosmic Ray Measurements With Transverse Muons

After preparing p-type CdTe:As, we began considering

CONCLUSIONS

- BaF_2 is an intrinsically radiation-hard material, especially in the ultraviolet.

- Radiation-induced ultraviolet absorption bands are due to small concentrations of hydrogen/oxygen and transition-metal ions (Mn^{2+}).

Two ways to minimize radiation damage in BaF_2:

1. Continue to improve crystal growth procedures (progress is being made in this direction).

→ 2. Develop a post-growth procedure to remove unwanted impurities. One possibility is electrodiffusion, where an external electric field applied during irradiation drives impurities out of the crystal.

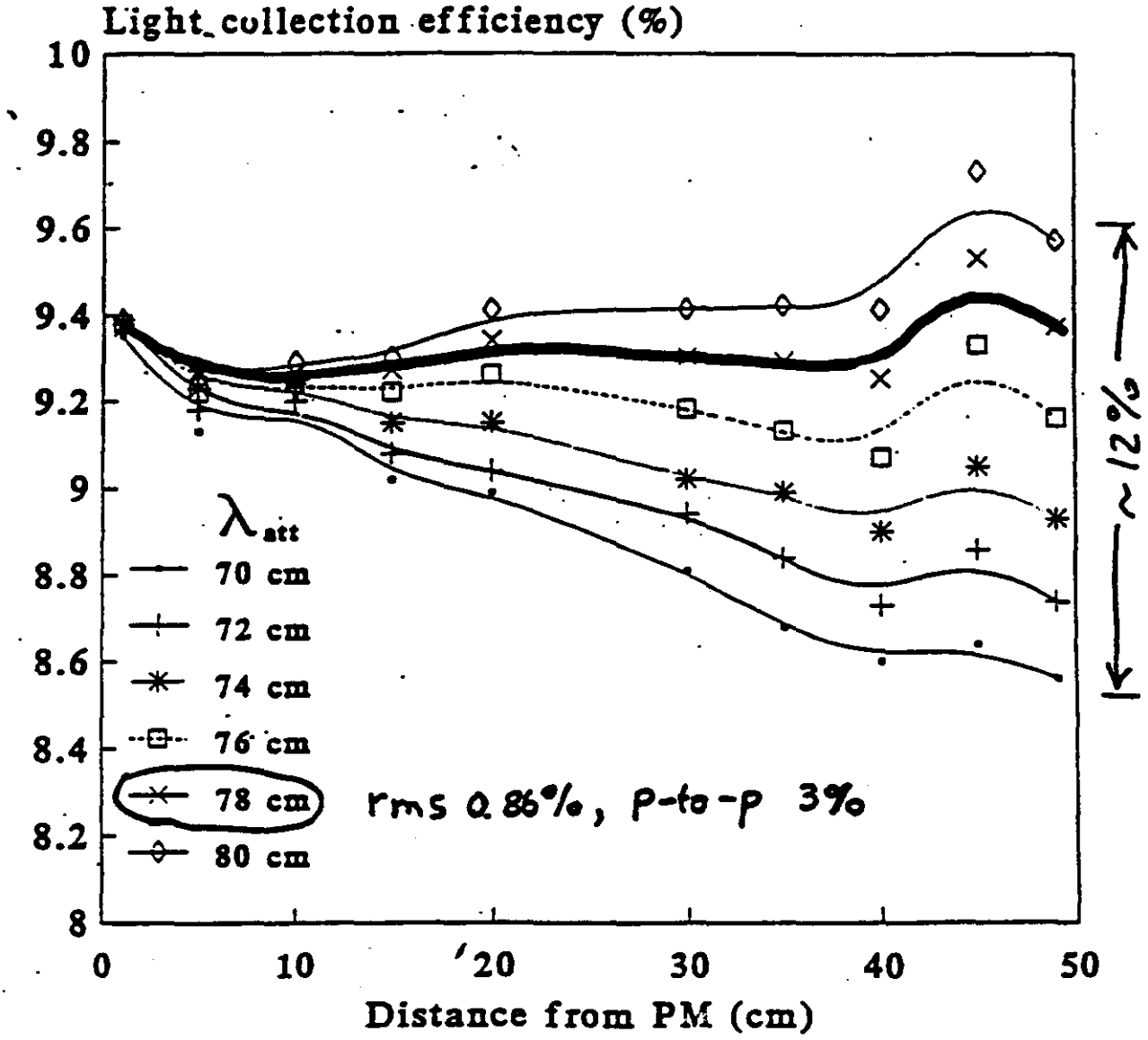
Sept.: IMPORTANT for further Outlook

Required L_{att}

(K. SHMAKOV)

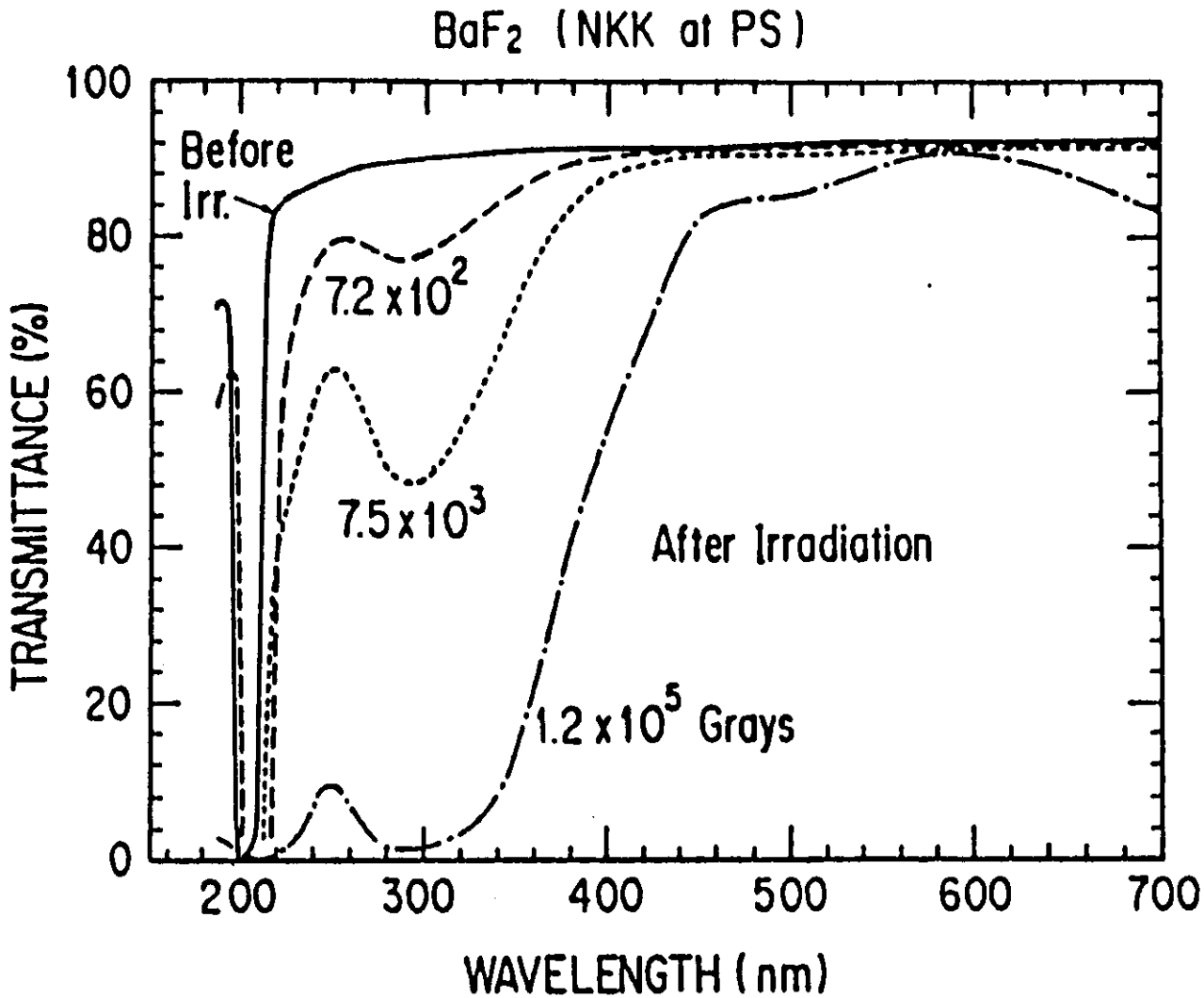
- Since the focusing effect and light absorption compete in the tapered crystals there is a minimal light attenuation length exist which can be compensated by focusing effect (plus crystal coating)
- For any light attenuation length larger than minimal the corresponding coating can be applie such that crystal response will be uniform
- If the light attenuation length would be the sam for all crystals (minimal spread from crystal to crystal) and coating properties would be perfectly reproducible it would be the simplest way to obtain uniform crystal response
- If light attenuation length is different from crystal to crystal the coating that match this particular attenuation length should be applied in a controlled way to obtain required uniformi
- It needs to be demonstrated that crystals in mas production have uniform properties (attenuatior length) and/or that coating is controlable to the accuracy that will allow to compensate variations of light attenuation length
- EXPERIENCE: CRYSTAL BALL
  L3
  CLEO II

Uniformity for different λ_{att} and transparent front facet (for side facets F=1.) MgF2(thin film) + Al coating



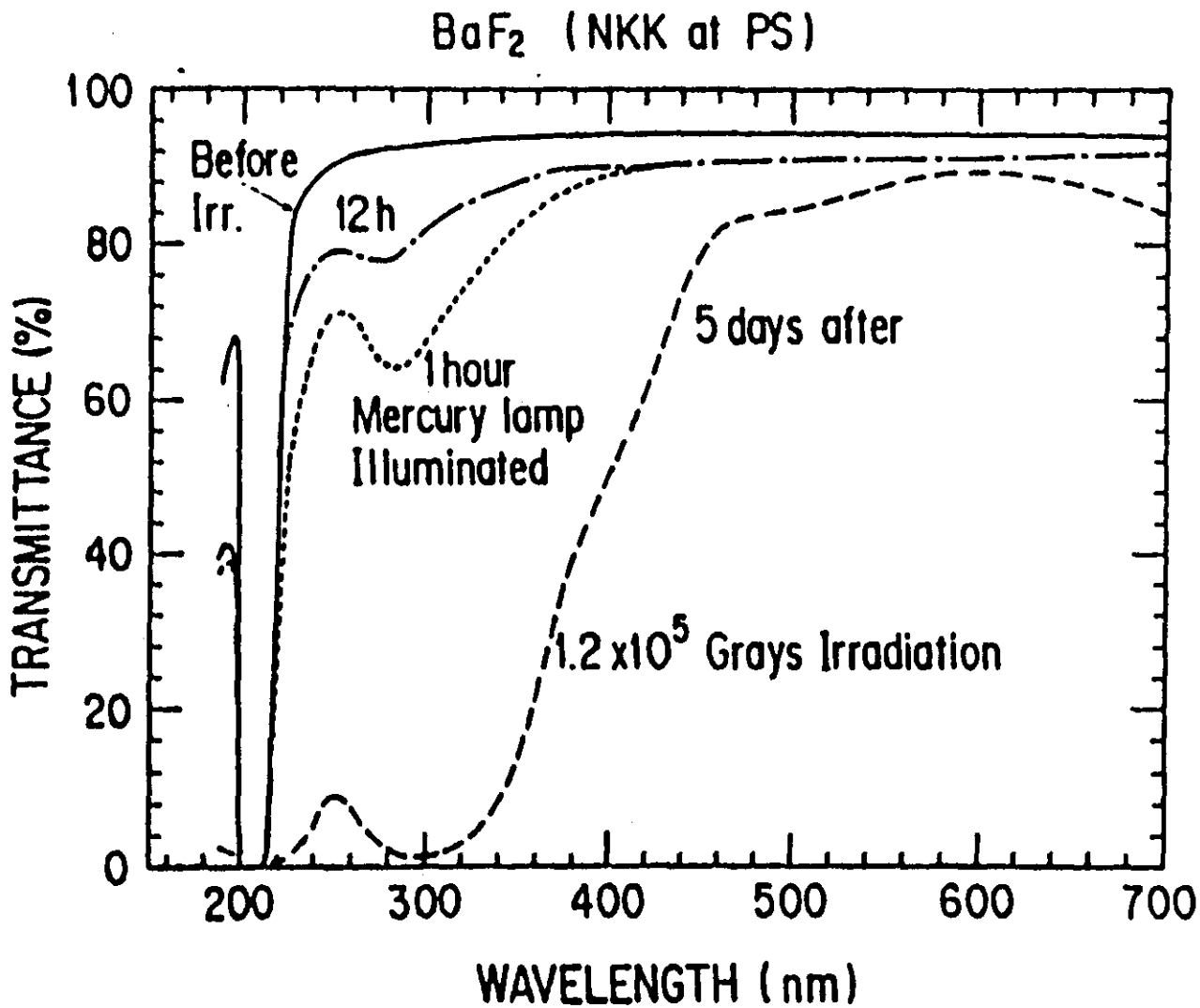
MURASHITA
et al.
1986
BaF_2 IRRAD.
With 12 GeV
PROTONS

LEAD ABSORP-
TION PEAK



Percent transmittance of BaF_2 (NKK) as a function of the wavelength with the radiation near the 12 GeV proton beam line. The lines are solid (before irradiation), dashed (7.2×10^2 Gy), dotted (7.5×10^3 Gy) and dash–dotted (1.2×10^5 Gy).

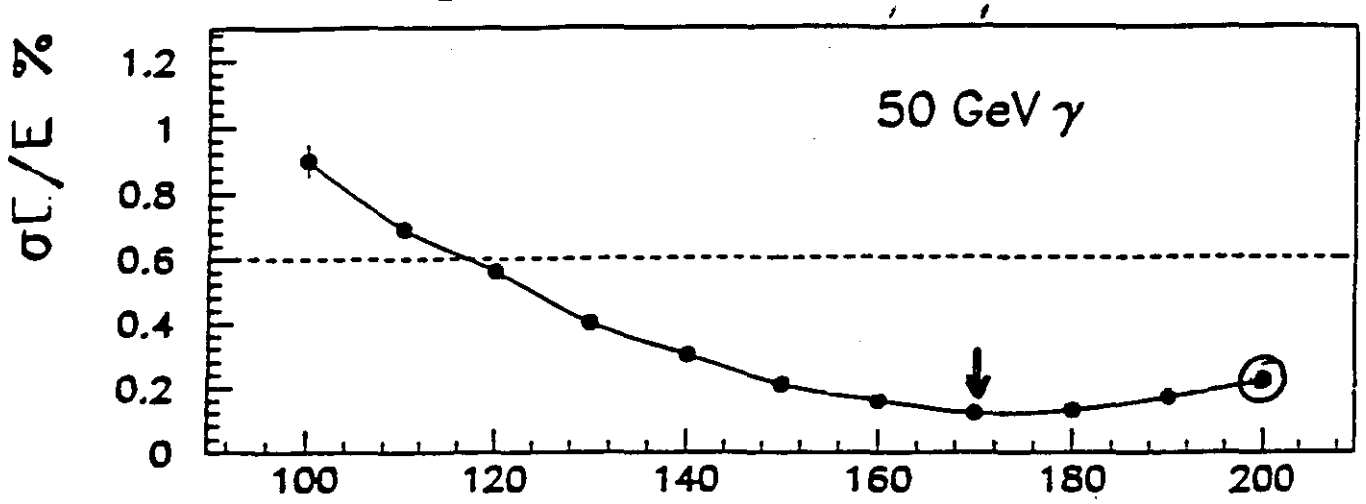
• Bleaching WITH UV



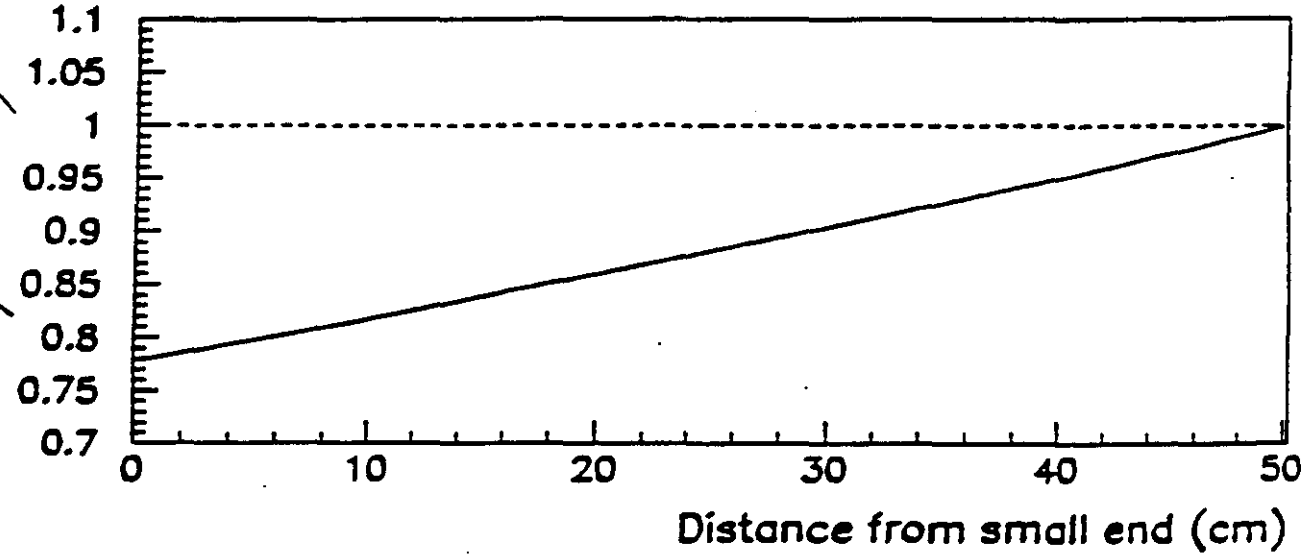
Recoveries of the transmittance in BaF_2 (NKK) with illumination of the mercury lamp after irradiation by 1.2×10^5 Gy. The lines are solid (before irradiation), dash–dotted (after illumination of 12 h), dotted (after illumination of 1 h) and dashed (before illumination.)

SCENARIO – all crystals were NOT preradiated

and were uniform with λ=200cm

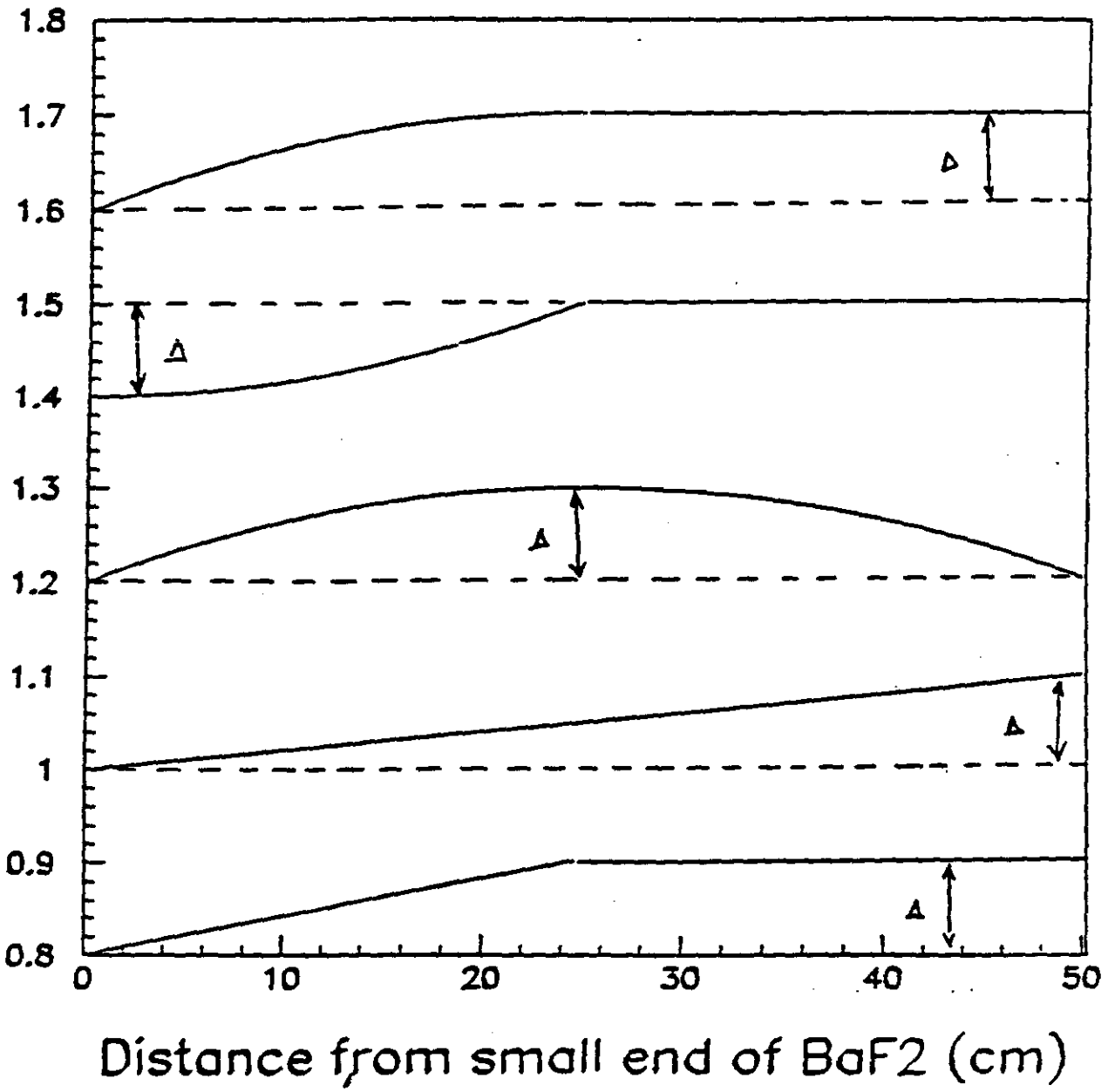


Attenuation length(cm) after irradiation

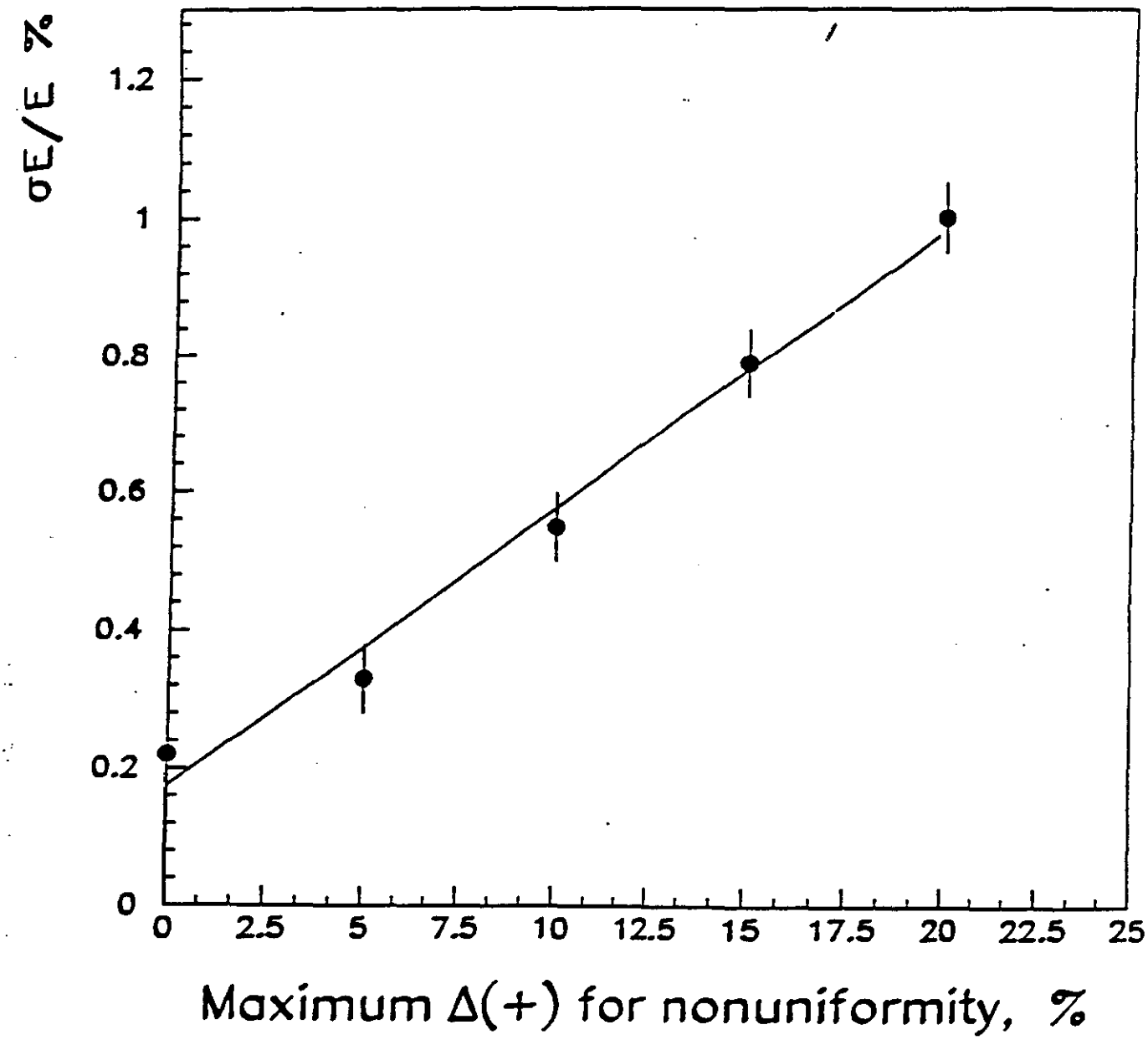


Nonuniformity for λ=100cm (at saturation)

5 TYPES of nonuniformities



ALL 5 TYPES of nonuniformities with positive slope



LIGHT COLLECTION NONUNIFORMITY CONTRIBUTION b_{NU}

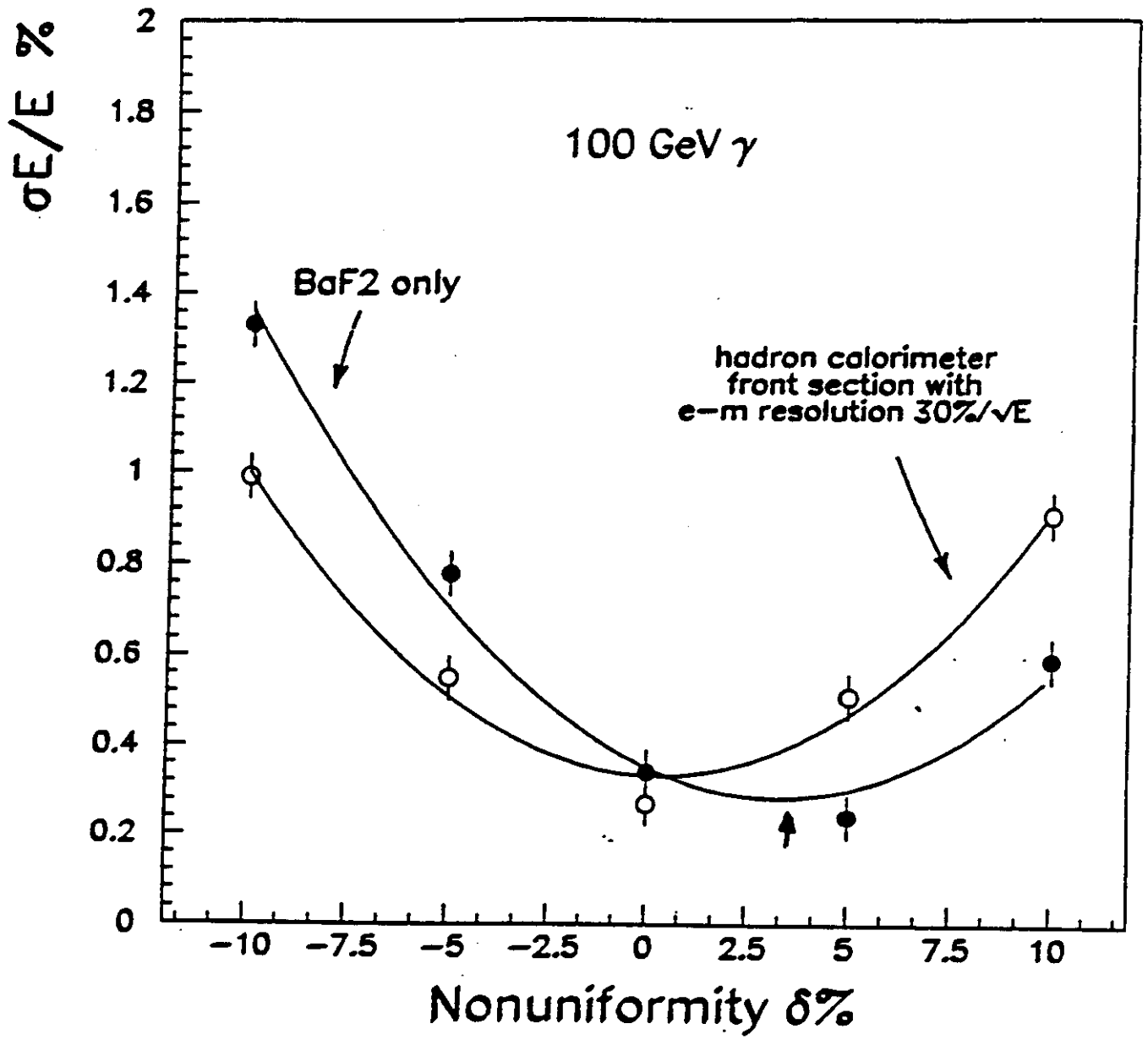
→ $\Delta^{(+)} \leq 5\%$ ⇒ $b_{NU} \leq 0.25\%$

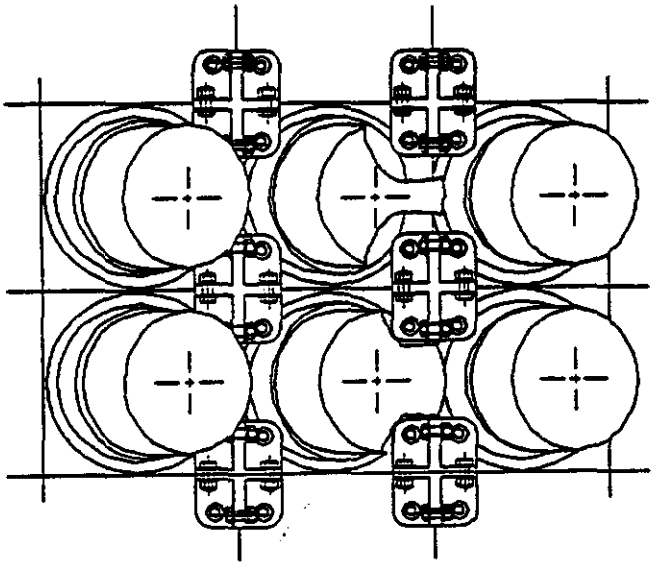
→ $\lambda = 200\,cm \rightarrow \gtrsim 150\,cm$

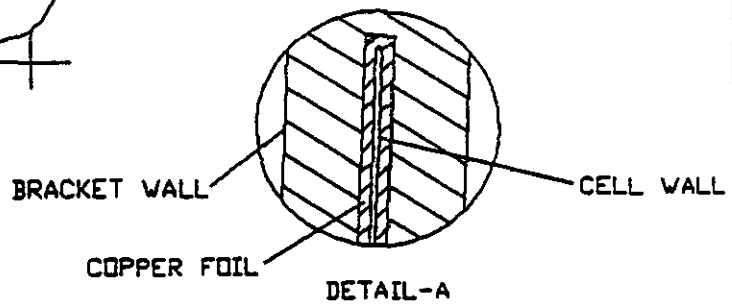
- Controlled by Light Annealing
- Compensation of Energy Leakage + enhanced Rear Response

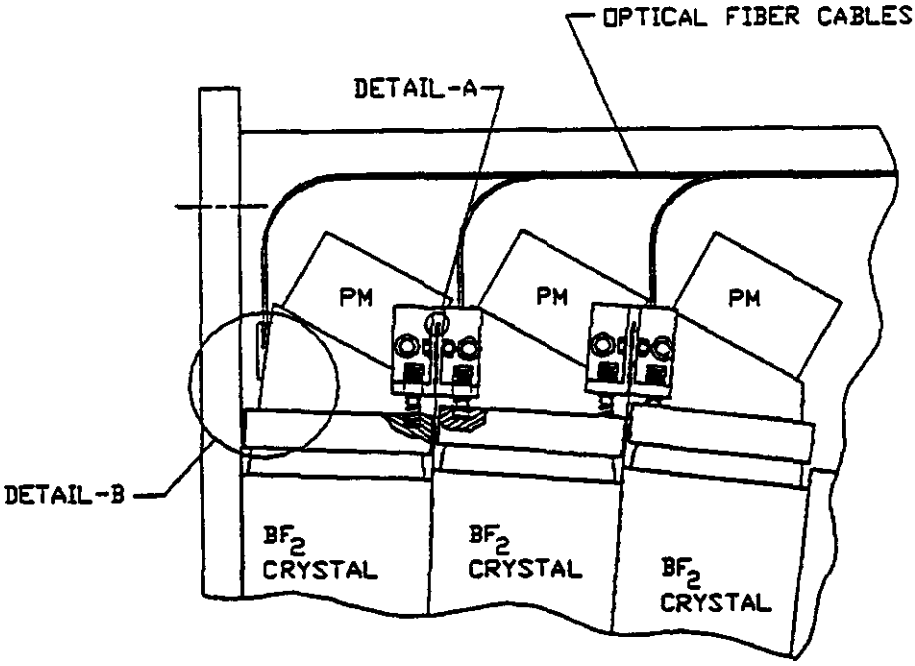
→ Overall $b_{NU} \approx 0.25\%$

BaF2 resolution vs nonuniformity slope (δ)

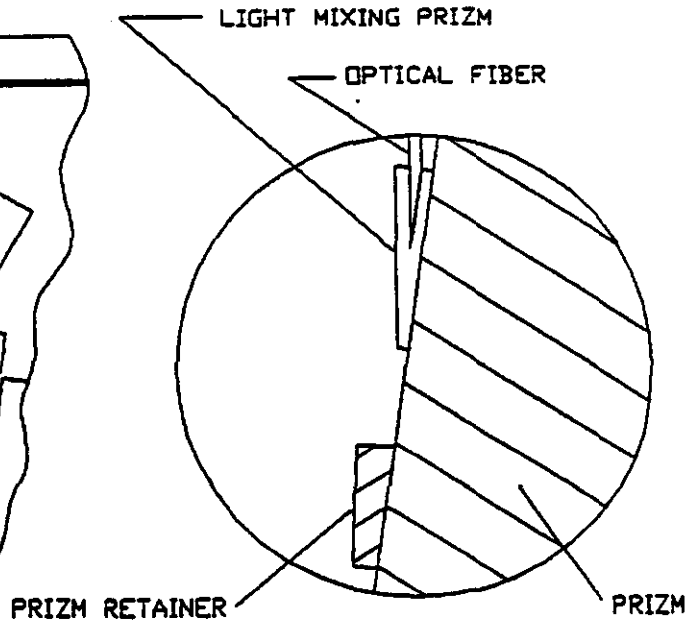








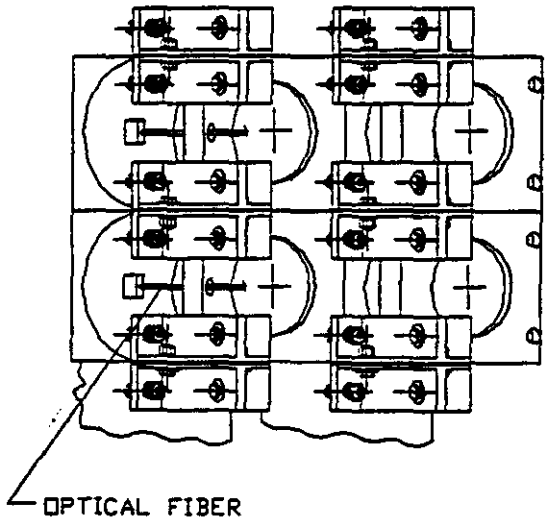
VIEW WITHOUT CELL WALL

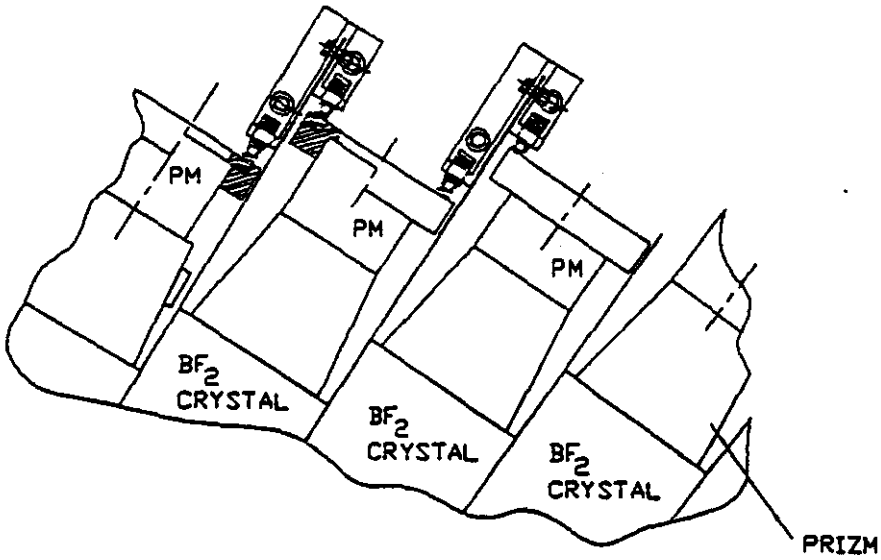


DETAIL-B

FIRST TYPE OF CRYSTAL FIXATION

ORNL



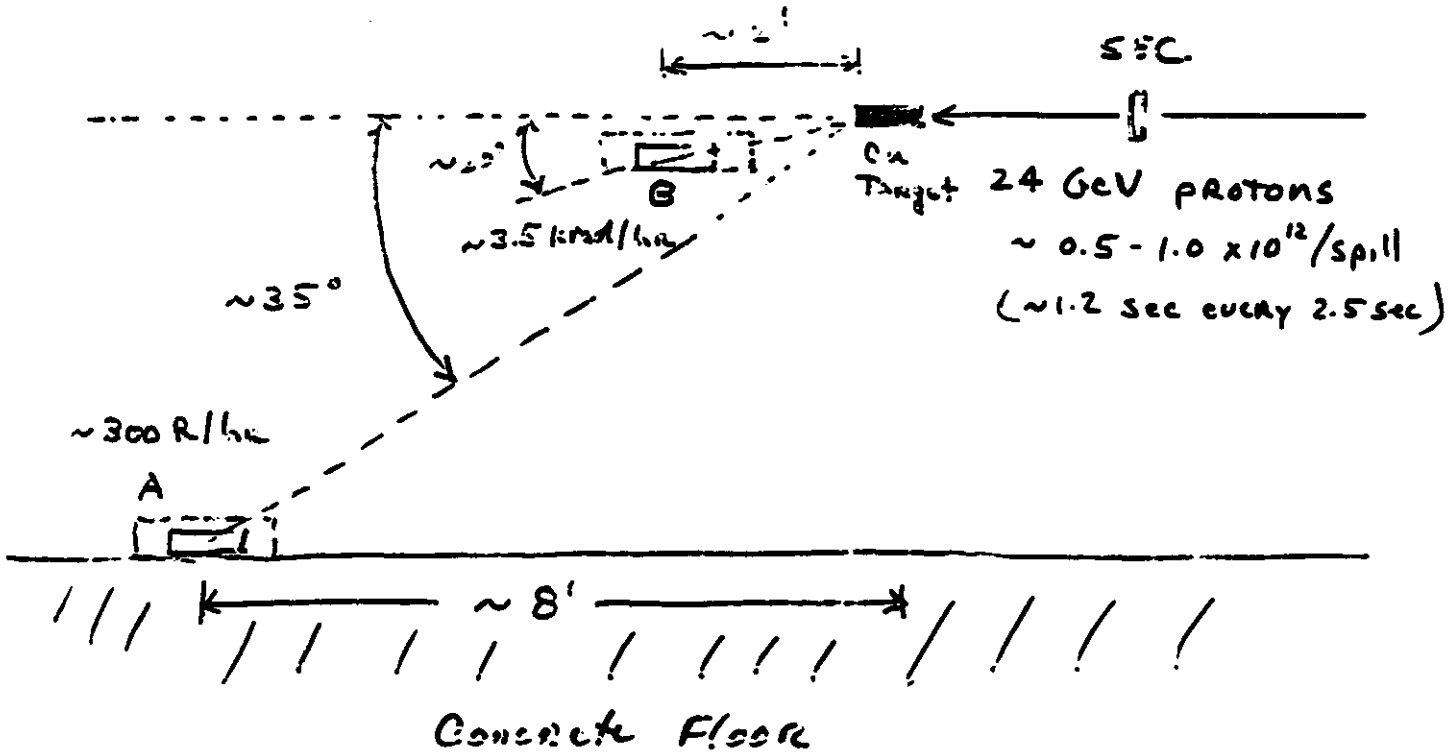


VIEW WITHOUT CELL WALL

SECOND TYPE OF CRYSTAL FIXATION

ORNL

AGS IRRADIATIONS



- Irradiations took place between 6/15 - 7/26
- Intermittent beam conditions (Real life!)
- Access required shutdown of entire AGS (all experiments and test beams - VERY UNPOPULAR!)
- Installation and removal of samples required access to high radiation area (typically few R/hr - DANGEROUS!)
- This was NOT a continuous exposure to pure hadrons (mixture of π^+, π^-, p, n and γ's - mainly from π^0's)
- Average energies ~ few GeV (much lower than SSC)
- Dose rate measured in LiF dosimeters for D ≤ 100 krad
- For D > 100 krad, SEC was used to extrapolate LiF dose
- Dose (MeV/kg) in BaF_2 ~ 4x dose in LiF

R & D Progress at CALTECH

R. Y. Zhu

BaF_2 Expt Meeting, SSCL

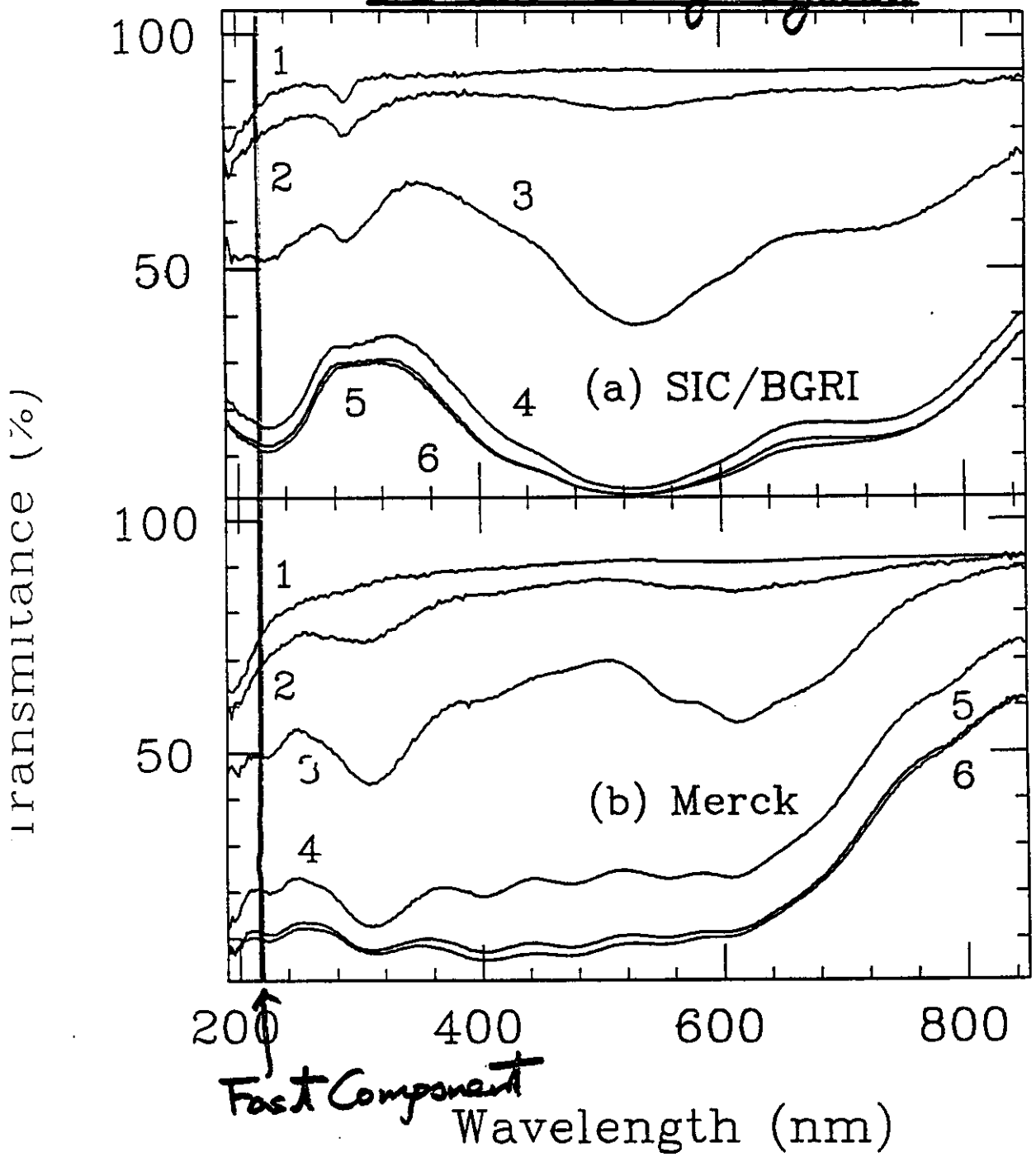
August 31, 1990

- New Crystals:
  - SIC;
  - OPTOVAC;
  - Russia ...
- Optical Bleaching in situ.

May. 1991

Radiation Damage of BaF$_2$ (I)

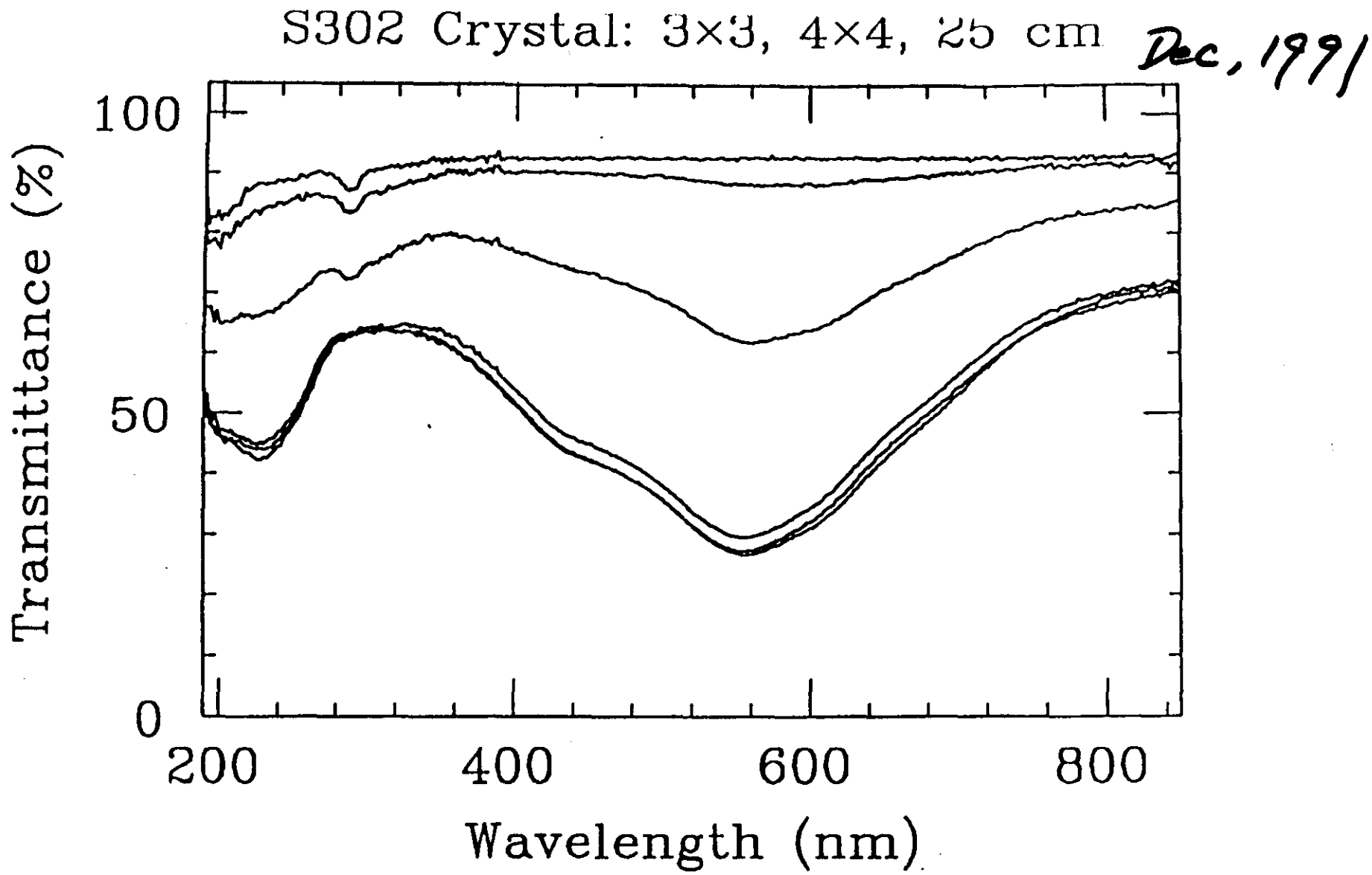
25 Cm long Cystal



2 : 100 Rads ; 5. 100 kRads

3 : 1kRads ; 6. 1 MRads.

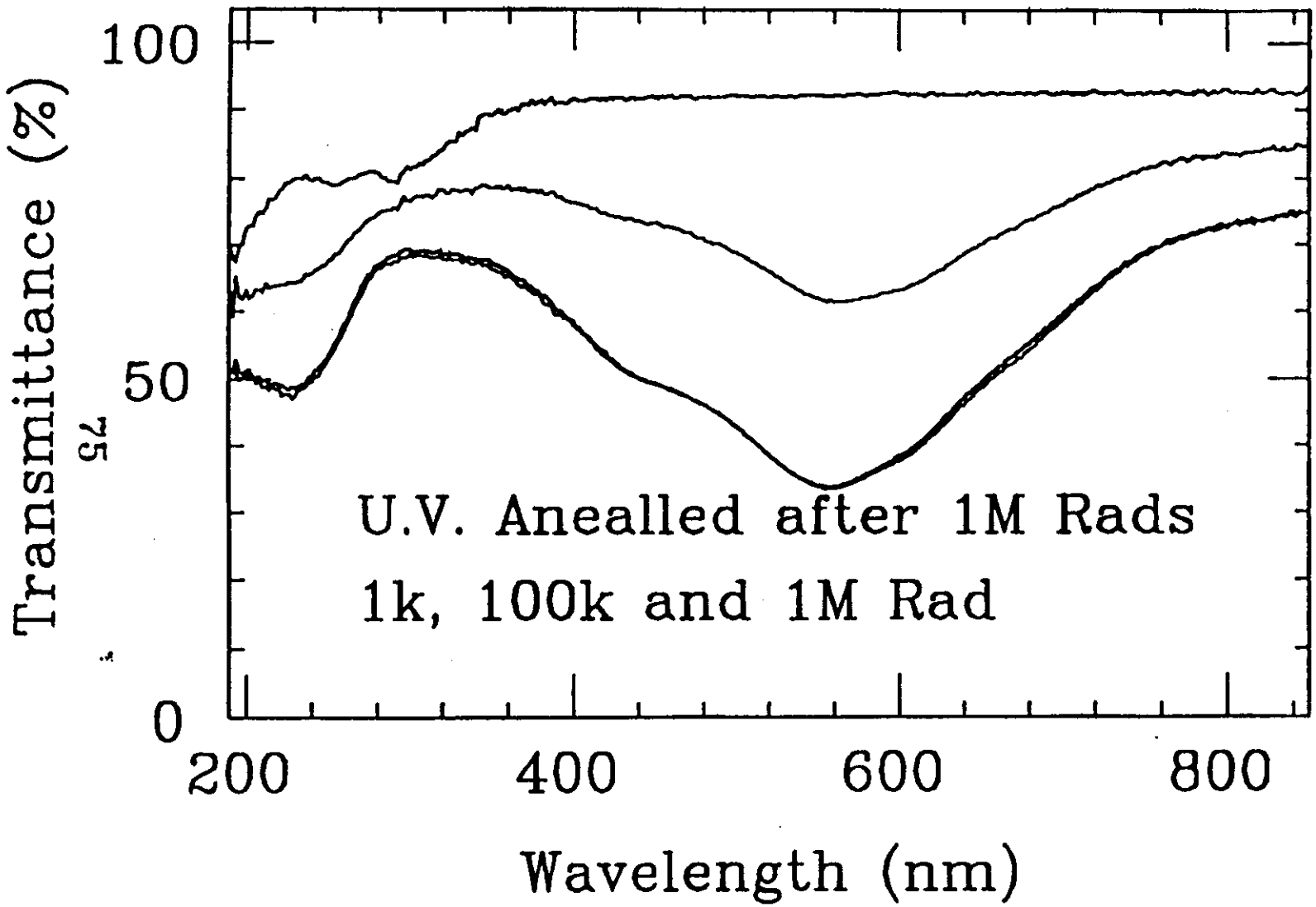
4 : 10kRads.



Sequence of Spectra in above figure:
Up to down: Before Irradiation,
100, 1k, 10k, 100k and 1M Rad

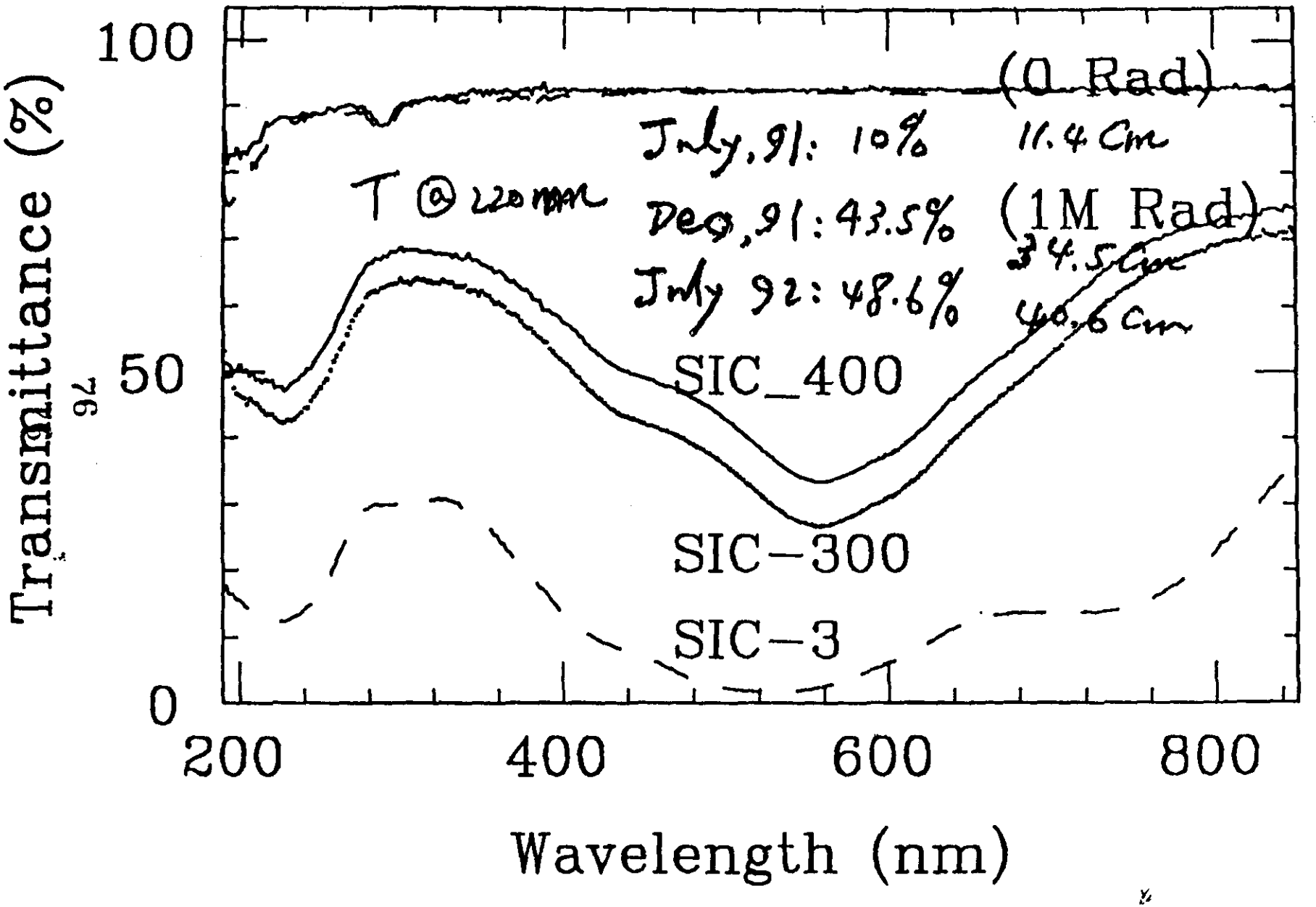
July 1992

S402: 3.6×3.6, 4.6×4.6, 25 cm



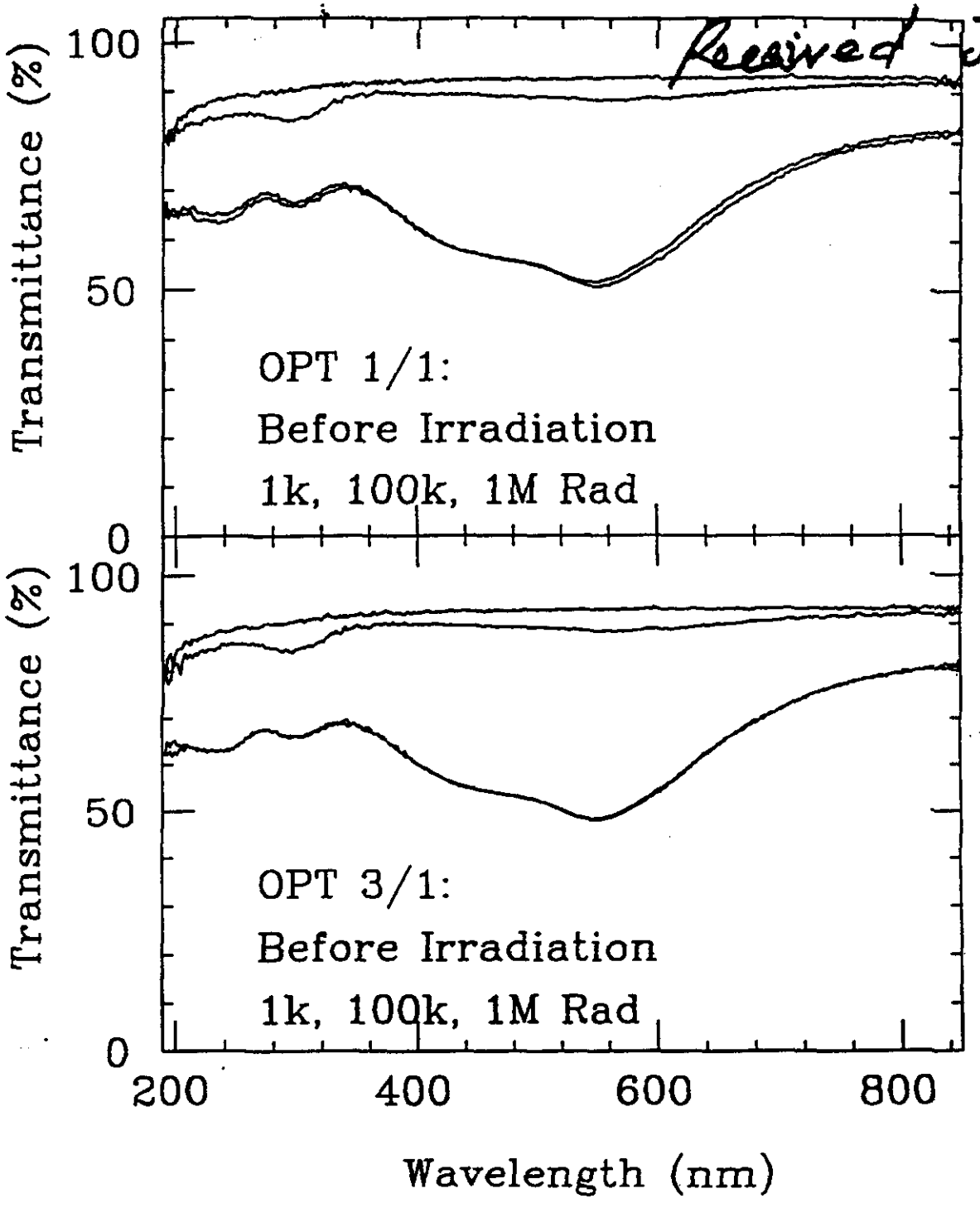
Comparison of SIC Crystals

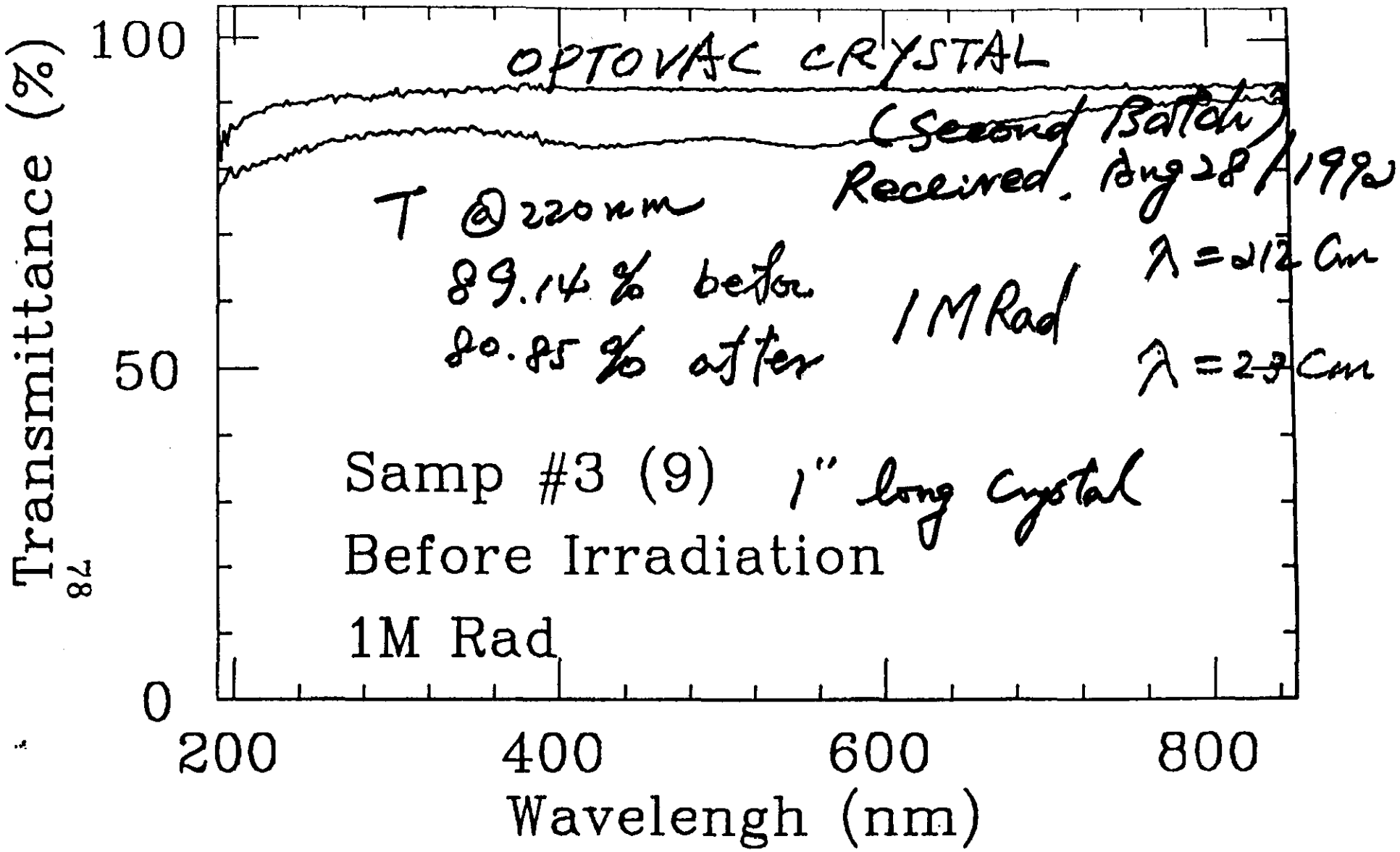
SIC Crystals' Development:



2 OPT Crystals: $\phi 2.5 \times 2.5$ cm (First Batch,

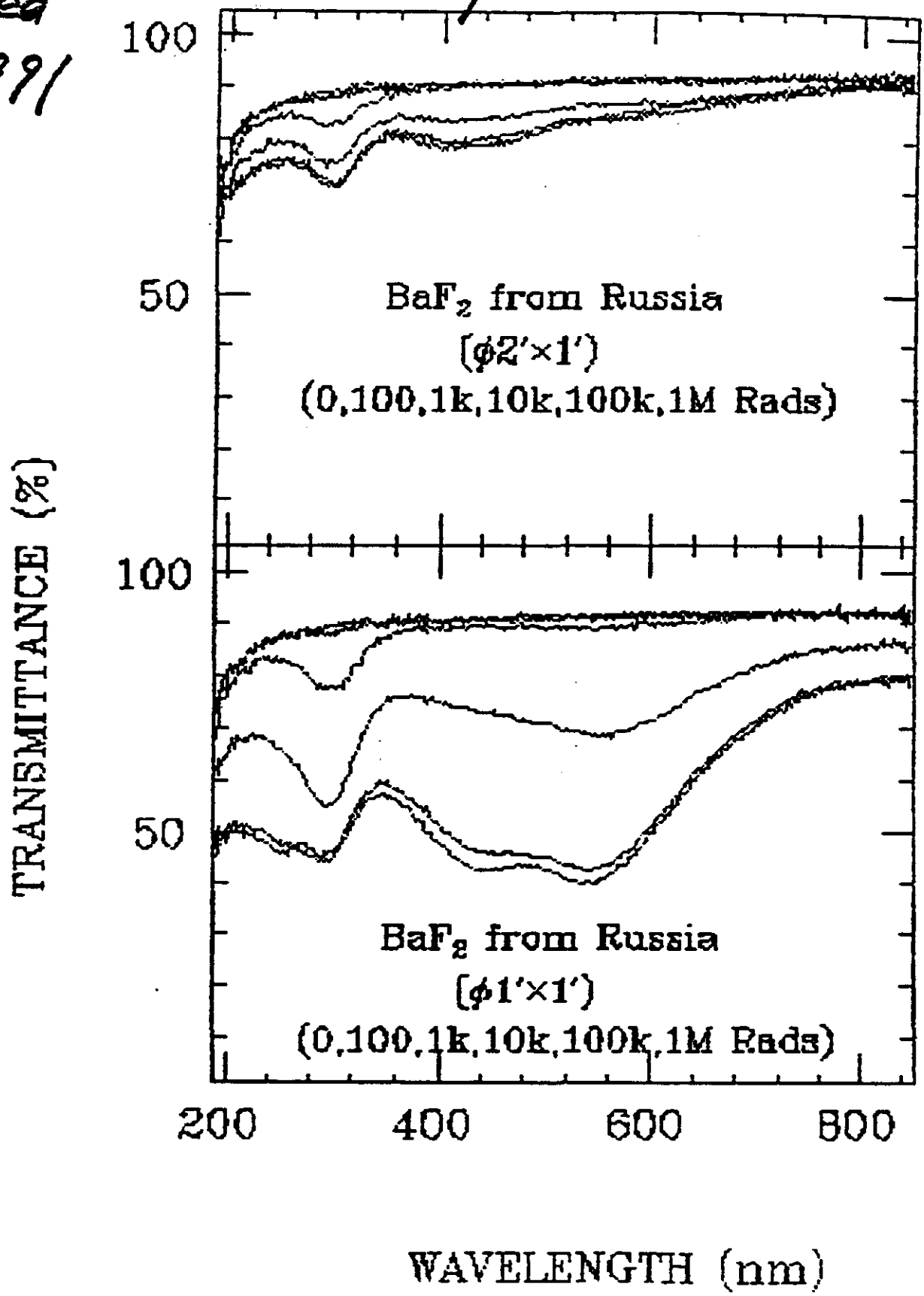
Received Jan, 1992




OPTOVAC CRYSTAL
(Second Batch)
Received. Aug 28 / 1992
T @ 220 nm
89.14 % before
80.85 % after
1 M Rad
λ = 212 Cm
λ = 23 Cm
Samp #3 (9)
1" long Crystal
Before Irradiation
1M Rad
Transmittance (%)
100
50
0
200
400
600
800
Wavelengh (nm)

Received 1991

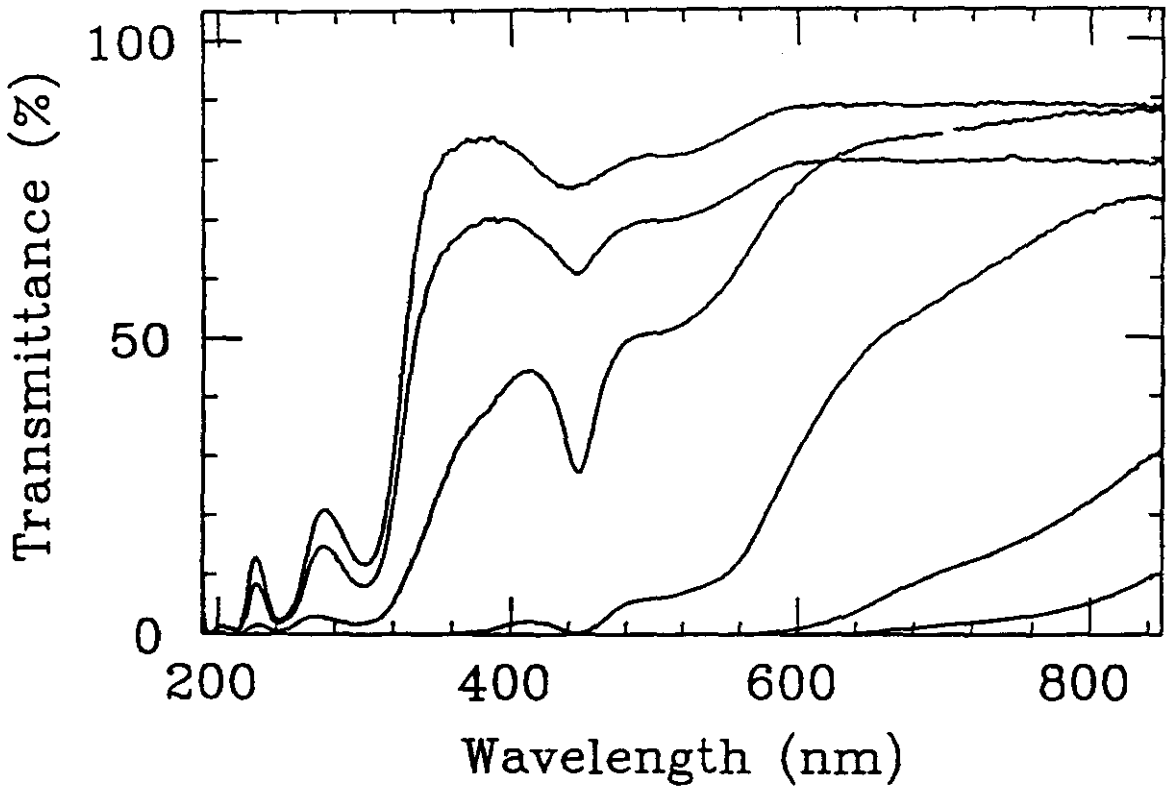
Russian Crystals from S.P.



Russian Crystal

Received May, 1992

RU1 Crystal: 13×31×290 mm

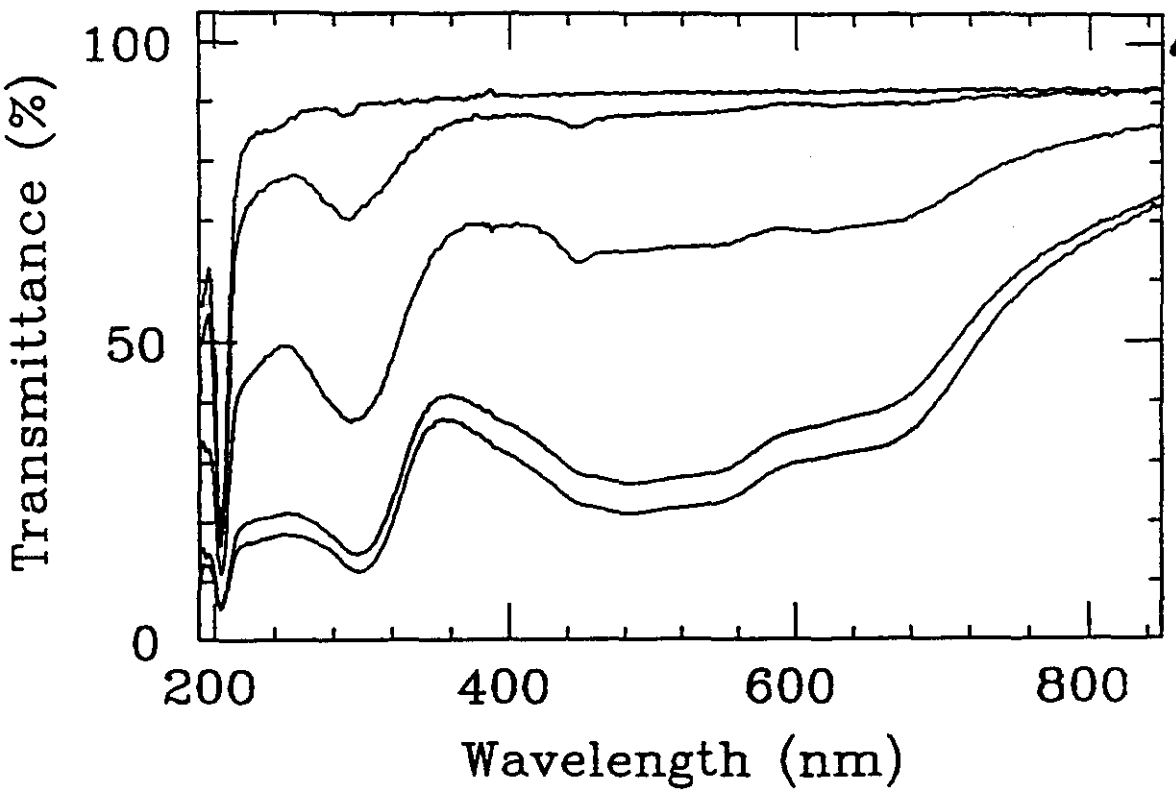


Sequence of Spectra in above figure:
Up to down: Before Irradiation,
100, 1k, 10k, 100k and 1M Rad

Russian Crystal

Received May. 92

RU3 Crystal: 4.4×4.4×5.4 cm

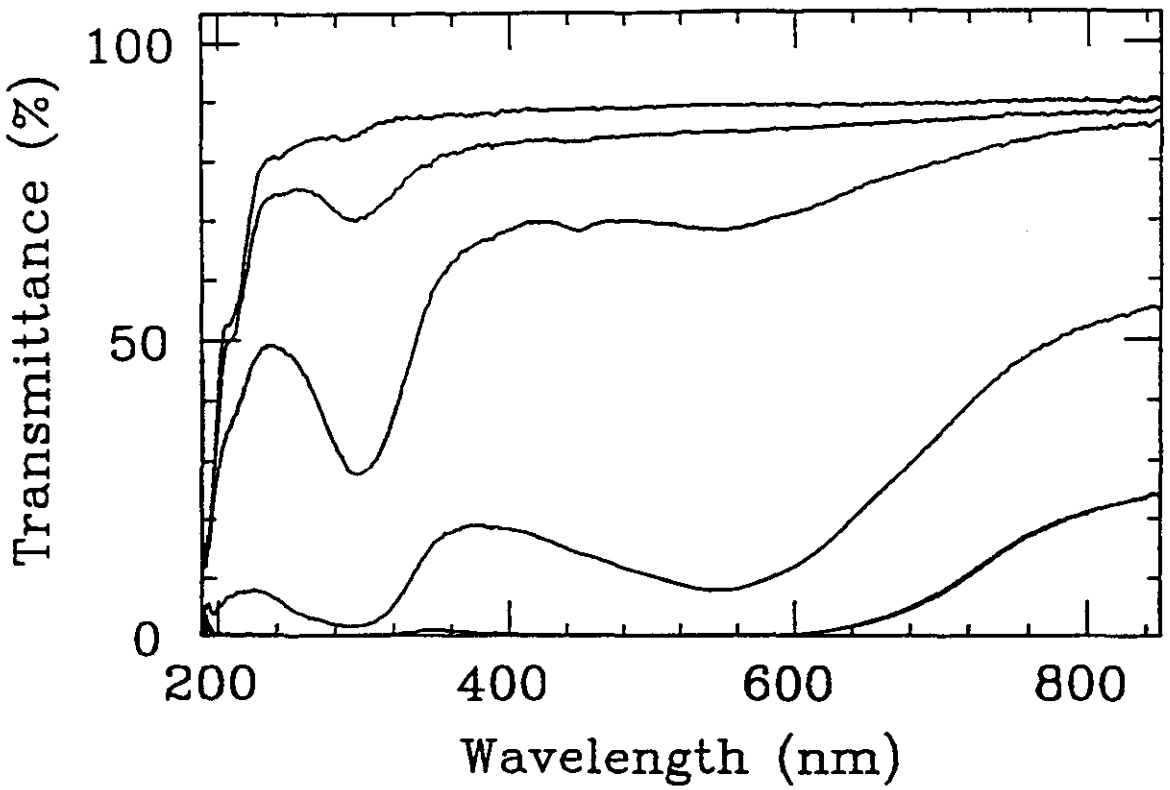


Sequence of Spectra in above figure:
Up to down: Before Irradiation,
1k, 10k, 100k and 1M Rad

Crystal from [illegible]

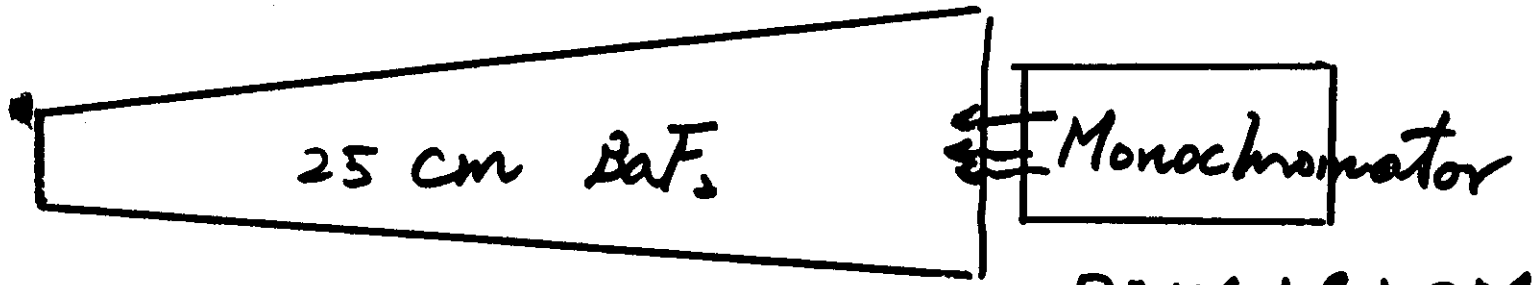
Received May, 9

CZ1 Crystal: 30×30×205 mm



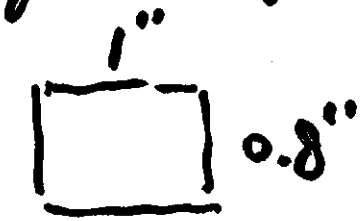
Sequence of Spectra in above figure:
Up to down: Before Irradiation,
100, 1k, 10k, 100k and 1M Rad

Optical Bleaching Setup

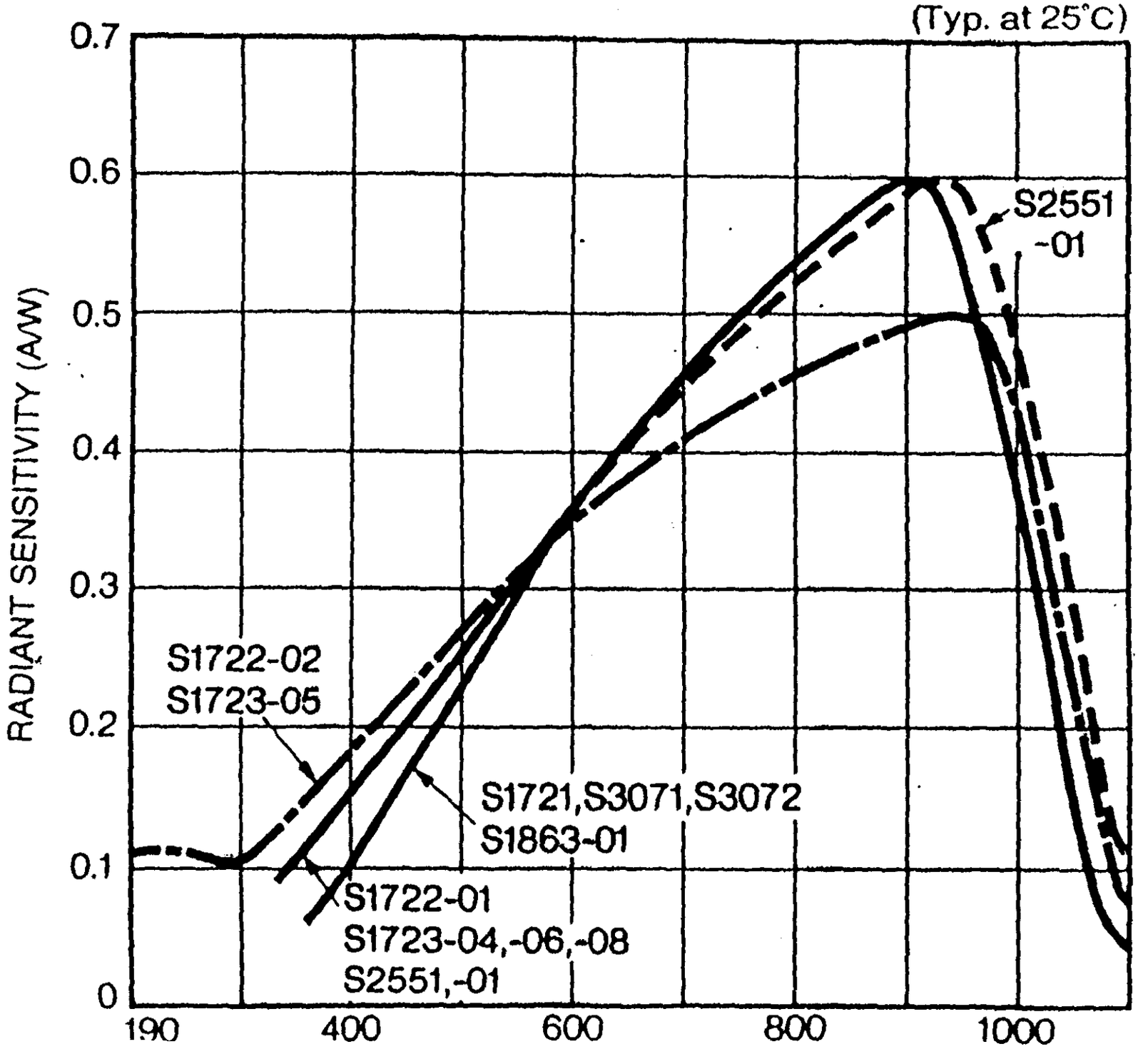


BAUCH & LOMB
Grating 1200 Groove/G
10 nm width

Light Spot



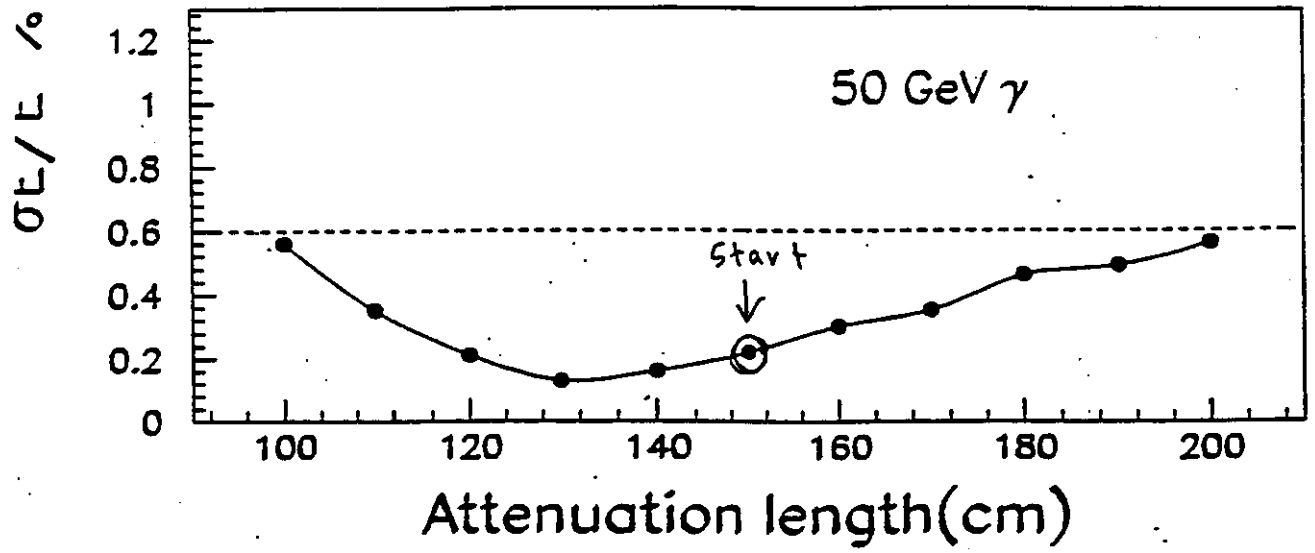
Spectral Response

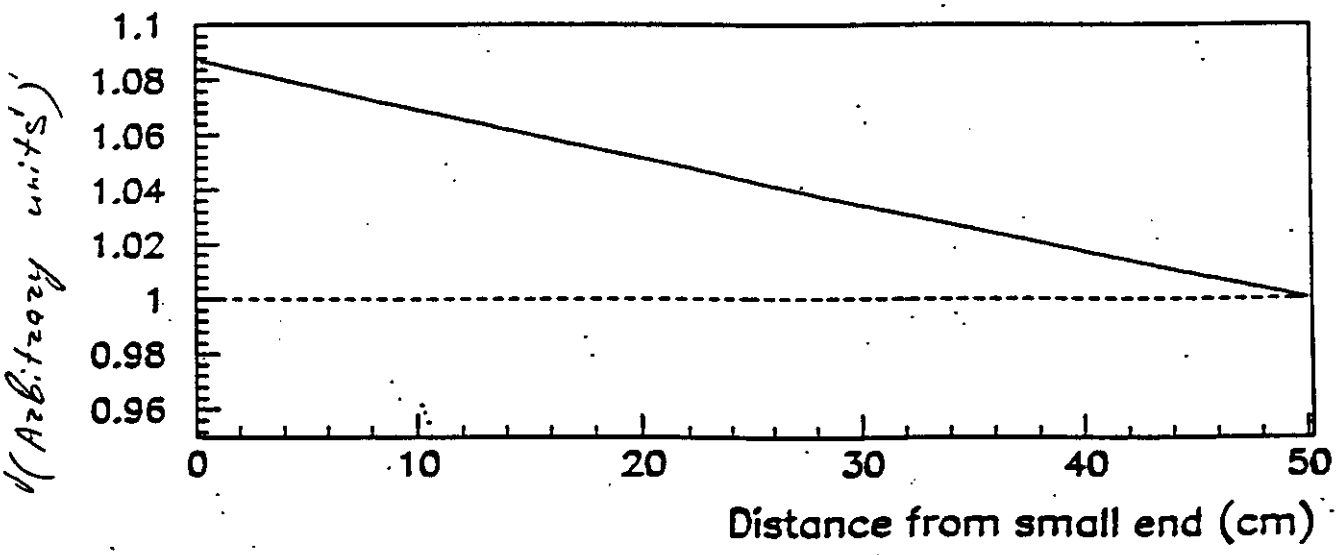


Annealing of CCC crystals

SCENARIO – all crystals were preradiated to λ=150cm

and were uniform with λ=150cm



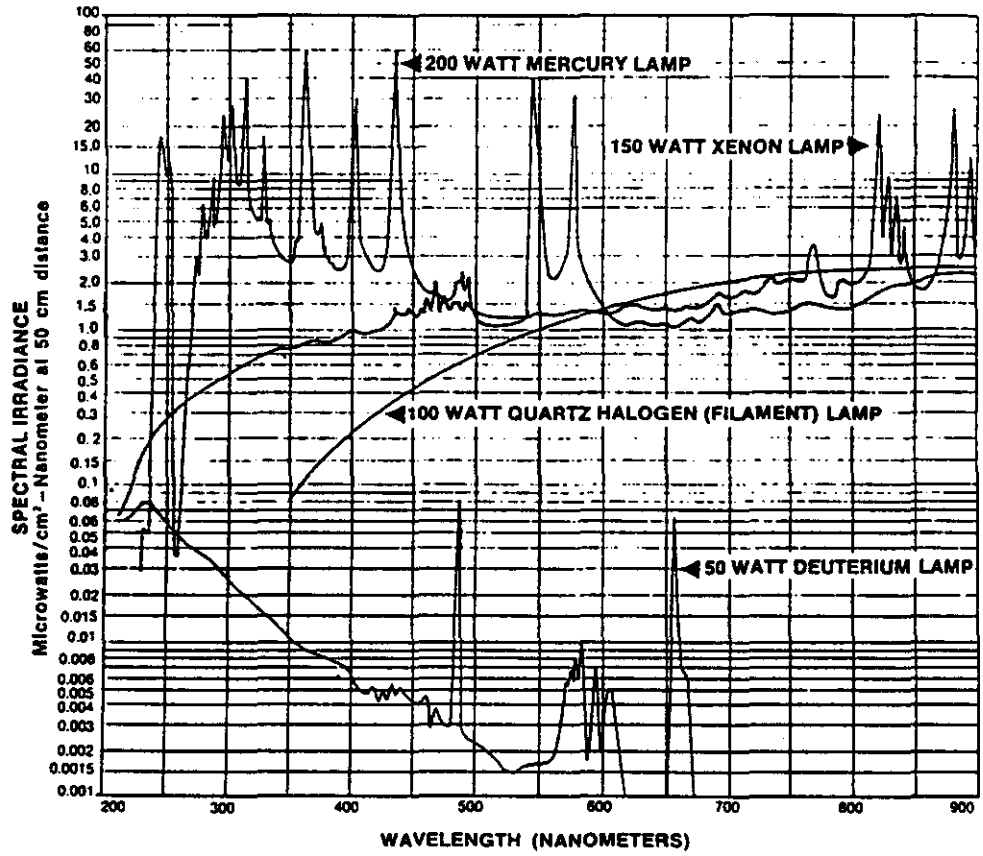


Nonuniformity for λ=200cm (after full recovering)

Fig 2-4

The absolute output spectra reproduced here were run in the Oriel Calibration Laboratory using spectral irradiance and thermopile standards traceable to N.B.S. Standards. This data should be regarded as typical and subject to variation from lamp to lamp. The instrument bandwidth is 2 Nanometers.

TYPICAL OUTPUT SPECTRA



TO ESTIMATE IRRADIANCE FROM OTHER LAMPS

6251 **75 watt Xenon:** multiply 150 W Xenon by 0.30

6281 **100 watt Mercury:** multiply 200 W Mercury by 0.26

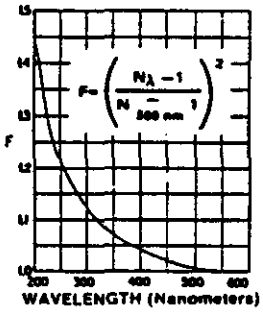
6285 **500 watt Mercury:** multiply 200 W Mercury by 2.85

POWER OUTPUT IN COLLIMATED BEAM

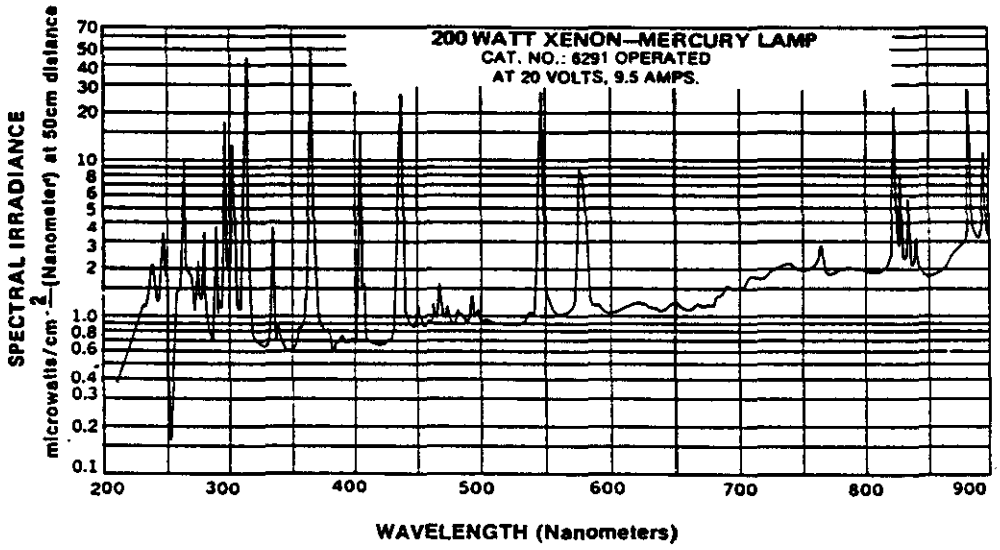
The units shown on the vertical axis are microwatts per cm²-nm at a distance of 50 cm. from the bare lamp. To convert this to power in the collimated beam from the source multiply by the factors listed below:

Source Model No.	Lens f/no.	To obtain approximate Collimated Beam Power in milliwatts per Nanometer multiply units shown by:
66006	f/1.5	0.65(F)
66007	f/1.0	1.15(F)
66009	f/0.7	2.0(F)

F gives effect to the lens focal length shortening at shorter wavelengths. This can be taken as 1.0 above 500. Below 500 nm it varies as follows:



This data does not include power recovered by the spherical reflector which will add 25 to 30%



Wavelength dependence of laser annealing

Renzheng Shang
Tsinghua Univ.
China

J. K P Lee McGill Univ.
Canada.

Aug 13,92

Dear Dr. Rencheng Shang,

Please find 3 crystals (BaF2) enclosed in the package, which are produced by Shanghai Institute of Ceramics (SIC).Following is a description of these crystals.

#S7 Crystal:

1. Size: ϕ25x25 (mm^3)
2. 2 top surfaces polished by SIC and then polished again by LLNL
3. Irradiated with the doses of 100,1k,10k,100k and 1000k Rad at Caltech as well tested for transmittance at each step
4. Current status: 1000k rads irradiated

#S105 Crystal:

1. Size: 25x25x25 (mm^3)
2. 2 surfaces polished by SIC
3. No irradiated yet

#S213 Crystal:

1. Size: 25x25x25 (mm^3)
2. All surfaces polished by SIC
3. No irradiated yet

Please give me a note if you have any question about it.

Best wishes,

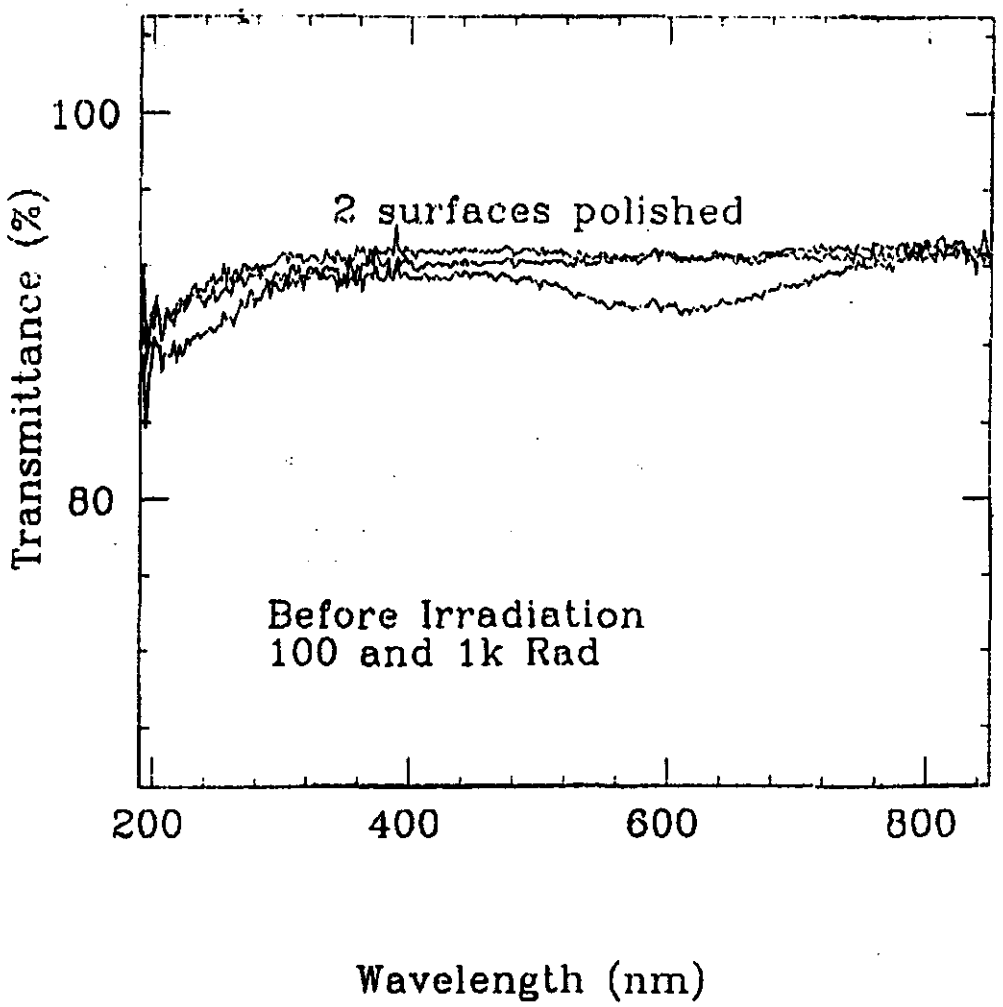
Da-an Ma

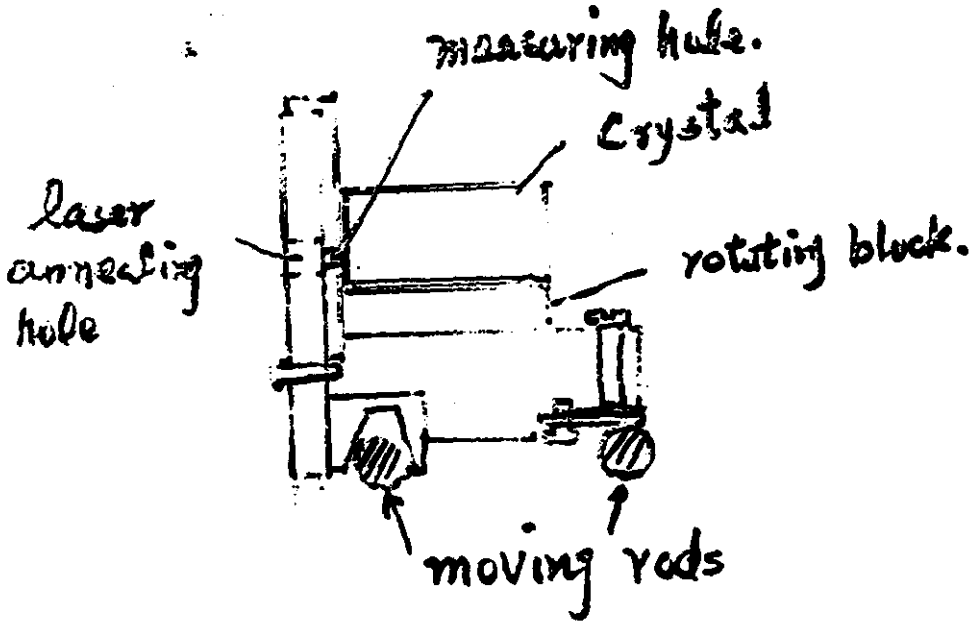
c.c. Dr. Renyuan Zhu

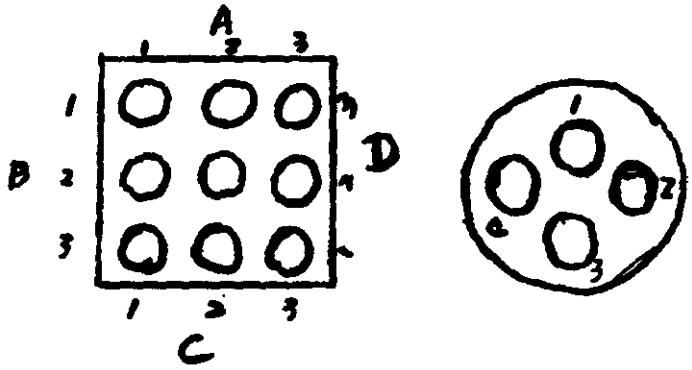
Addr. MS 256-48
California Institute of Technology
Pasadena CA 91125

Tel: 818 356-6657 Fax 818 795-3951

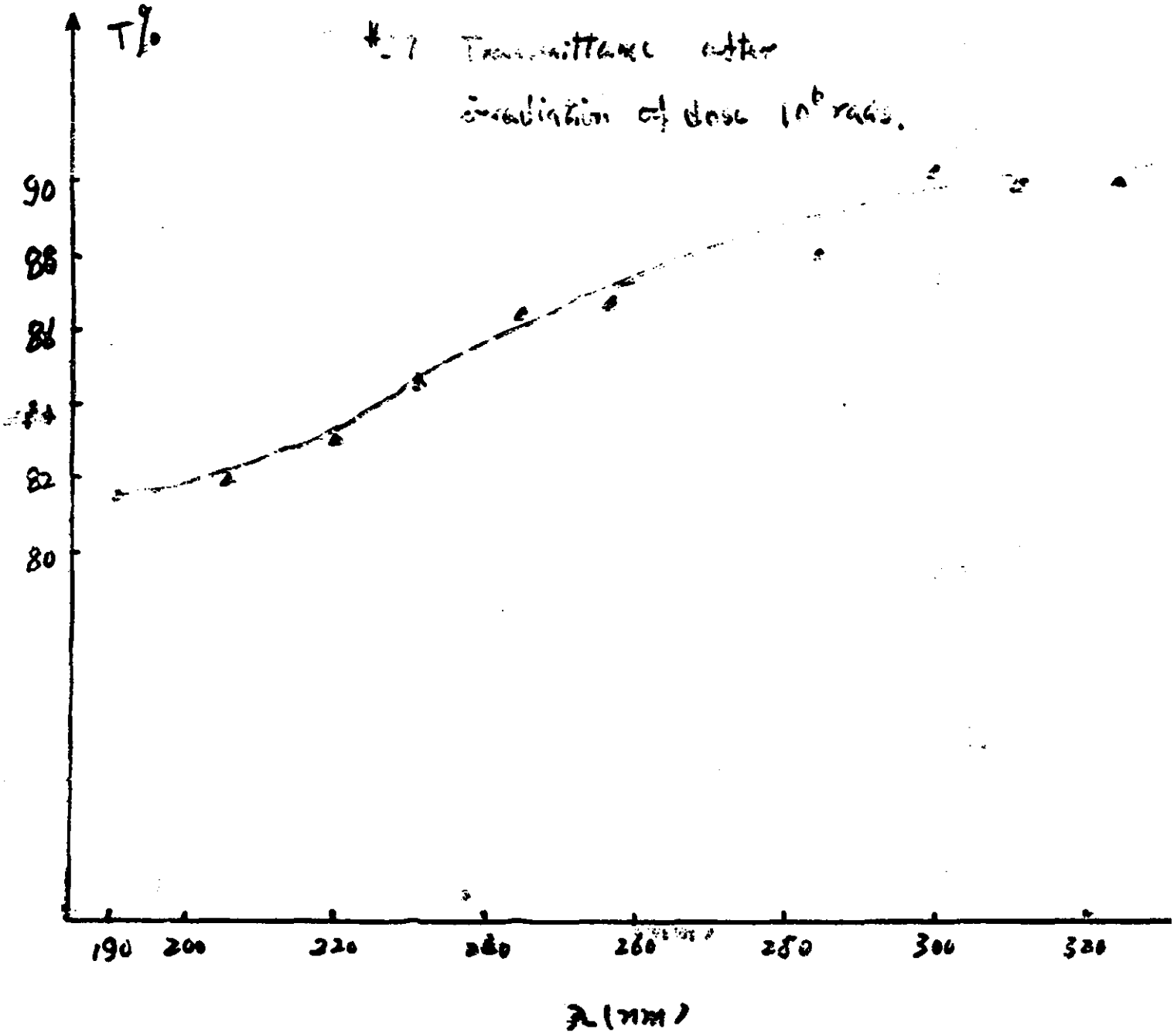
#S7: $\phi 25 \times 25$ (mm)



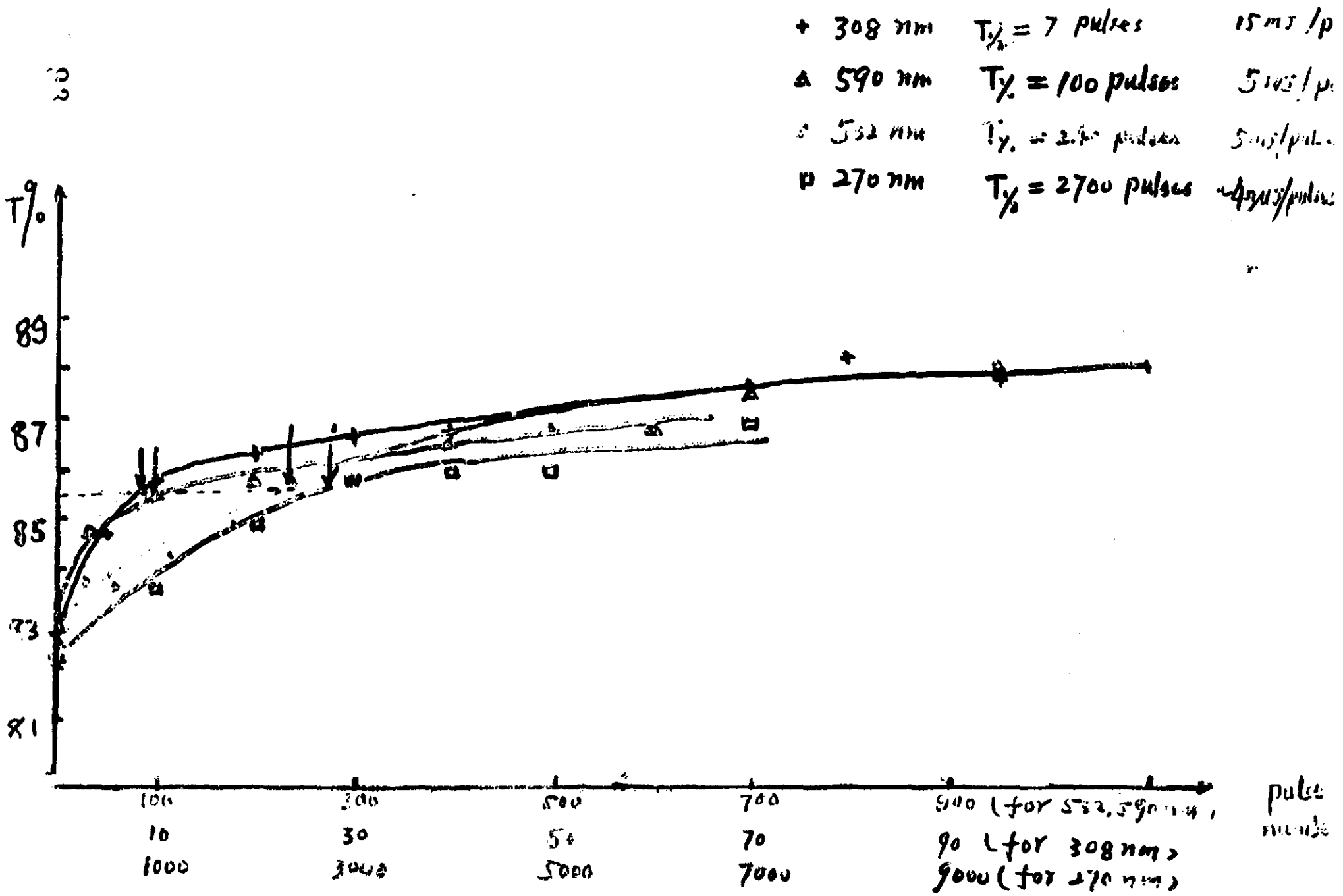




cubic cry. round cry.



#7 Transmittance after irradiation of dose 10^6 rads.



+ 308 nm T½ = 7 pulses 15 mJ/p
▲ 590 nm T½ = 100 pulses 5 mJ/p
532 nm T½ = 2.4 pulses 5 mJ/pul
□ 270 nm T½ = 2700 pulses ~4 μJ/pulse
T%
89
87
85
83
81
100
300
500
700
900 (for 532, 590 nm)
10
30
50
70
90 (for 308 nm)
1000
3000
5000
7000
9000 (for 270 nm)
pulse number

LASER ANNEALING RUN DATA

Run No.

1. 308nm position (3) 15mj/pulse
measuring 1 (218nm)

Pulse Number	0	1	5	10	20	30	40	60	80	100
Deposited Energy (mj)	0	15	75	150	300	450	600	900	1200	1500
Total Photon Number	0.0	2.3×10^{16}	1.2×10^{17}	2.3×10^{17}	4.6×10^{17}	6.9×10^{17}	9.2×10^{17}	1.4×10^{18}	1.9×10^{18}	2.3×10^{18}
T%	83.0	83.1	85.0	85.5	86.7	87.0	87.0	87.1	88.6	88.0

2. 590nm position (4) 5mj/pulse

Pulse Number	0	1	3	10	15	20	30	50	100	200	400
Deposited Energy (mj)	0	5	15	50	75	100	150	250	500	1000	2000
Total Photon Number	0.0	1.5×10^{16}	4.4×10^{17}	1.5×10^{17}	2.1×10^{17}	3.0×10^{17}	4.5×10^{17}	7.5×10^{17}	1.5×10^{18}	3×10^{18}	6×10^{18}
T%	83.0	83.7	82.4	84.2	83.9	84.6	85.0	85.2	85.8	86.0	87.0

3. 532nm position (2) 5mj/pulse

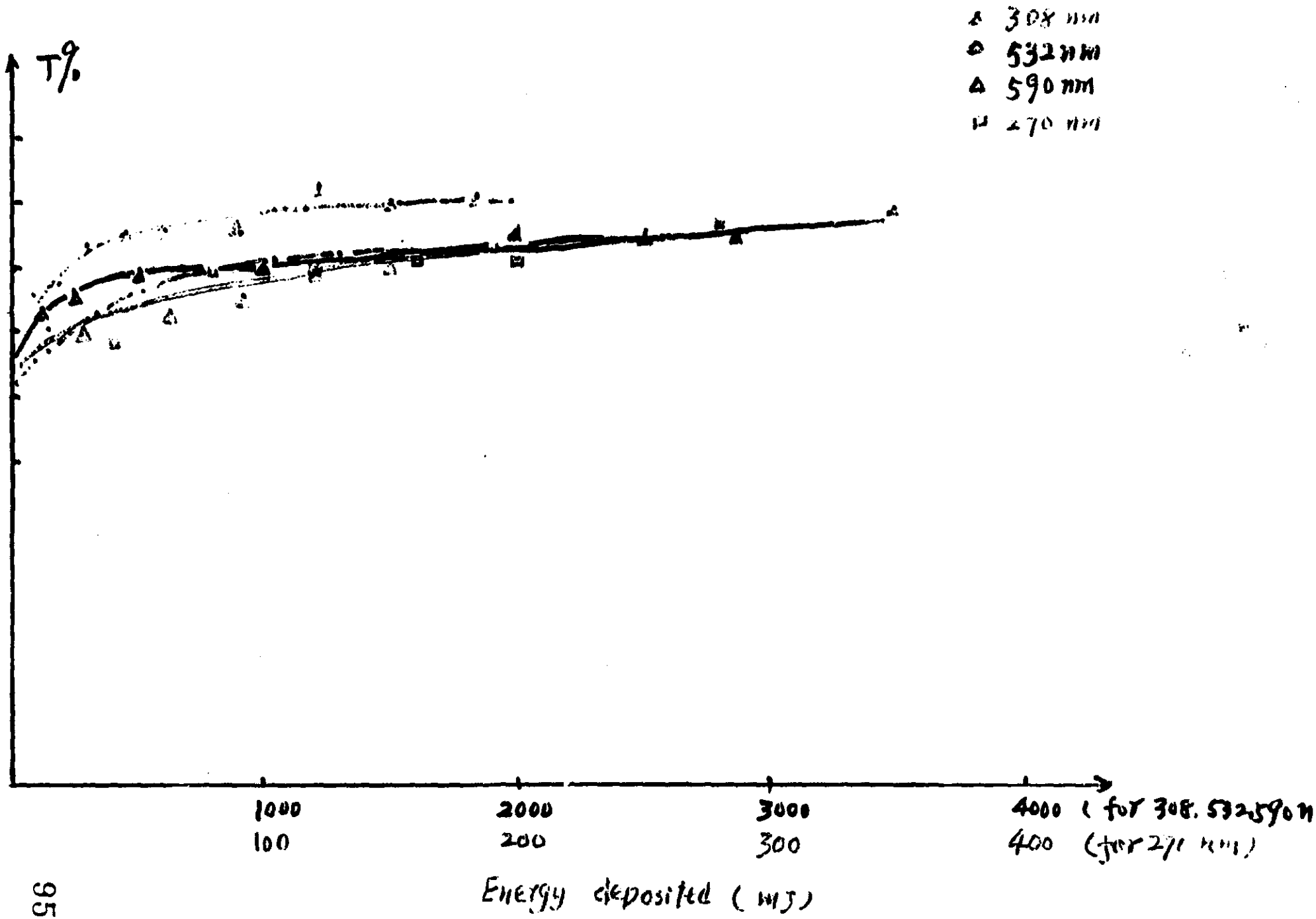
Pulse Number	0	10	30	60	120	180	240	300	500	700	1000
Deposited Energy (mj)	0	50	150	300	600	900	1200	1500	2500	3500	5000
Total Photon Number	0.0	1.3×10^{17}	4.0×10^{17}	8.0×10^{17}	1.6×10^{18}	2.4×10^{18}	3.2×10^{18}	4.0×10^{18}	6.7×10^{18}	9.3×10^{18}	1.3×10^{18}
T%	83.0	84.0	84.0	83.8	84.4	85.0	86.0	85.9	87.0	87.8	88.0

4. 270nm position (1) ~ 40mj/pulse

Pulse Number	0	1000	2000	3000	4000	5000	7000
Deposited Energy (mj)	0	40	80	120	160	200	280
Total Photon Number	0.0	5.4×10^{17}	1.1×10^{18}	1.6×10^{18}	2.2×10^{18}	2.7×10^{18}	3.8×10^{18}
T%	82.6	83.8	85.2	86.0	86.2	86.1	87.2

5. 1060nm position (1) 20mj/pulse

Pulse Number	0	1	5	10	20	40	60	100	200	500	1000
Deposited Energy (mj)	0	20	100	200	400	800	1200	2000	4000	10000	20000
Total Photon Number	0.0	1.1×10^{17}	5.3×10^{17}	1.1×10^{18}	2.1×10^{18}	4.2×10^{18}	6.3×10^{18}	1.1×10^{19}	2.1×10^{19}	5.3×10^{19}	1.1×10^{20}
T%	82.6	82.4	83.0	82.4	82.6	83.0	83.4	83.7	83.2	83.0	83.2


T%
308 nm
532 nm
590 nm
270 nm
1000
2000
3000
4000 (for 308, 532, 590 n
100
200
300
400 (for 270 nm)
Energy deposited (mJ)

Yu. Kamyshkov
Aug. 31, 92

Coatings

Types:

1. MgF_2 + Al
2. Pure Al
3. Absorbing masking
4. Diffusive (like L3 BGO)

Modes:

a. adjustable density constant over the crystal surface

b. density variable over the crystal surface

not tried

Uniformity for different λ_{att} and transparent front facet (for side facets F=1.) MgF2(thin film) + Al coating

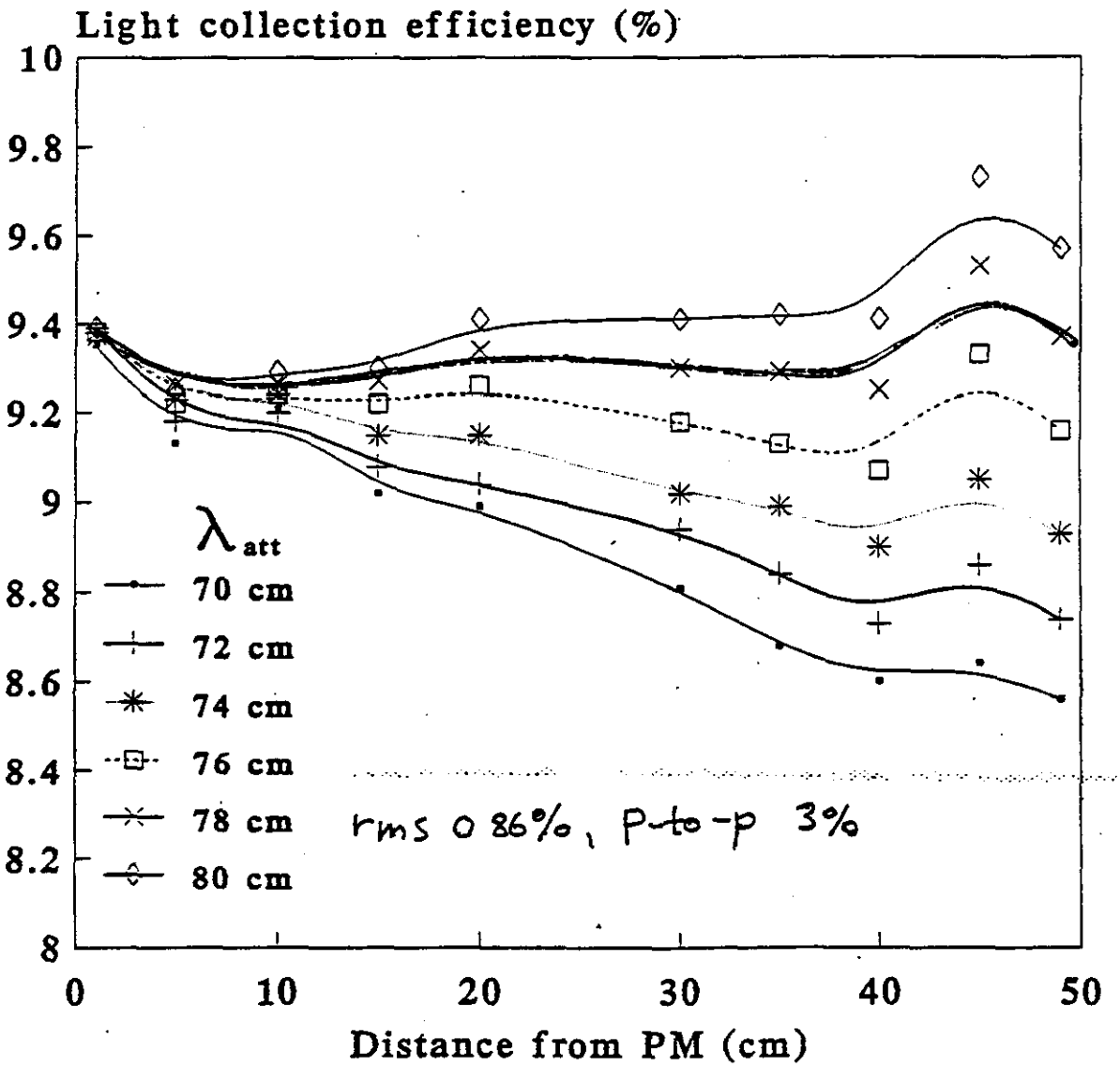
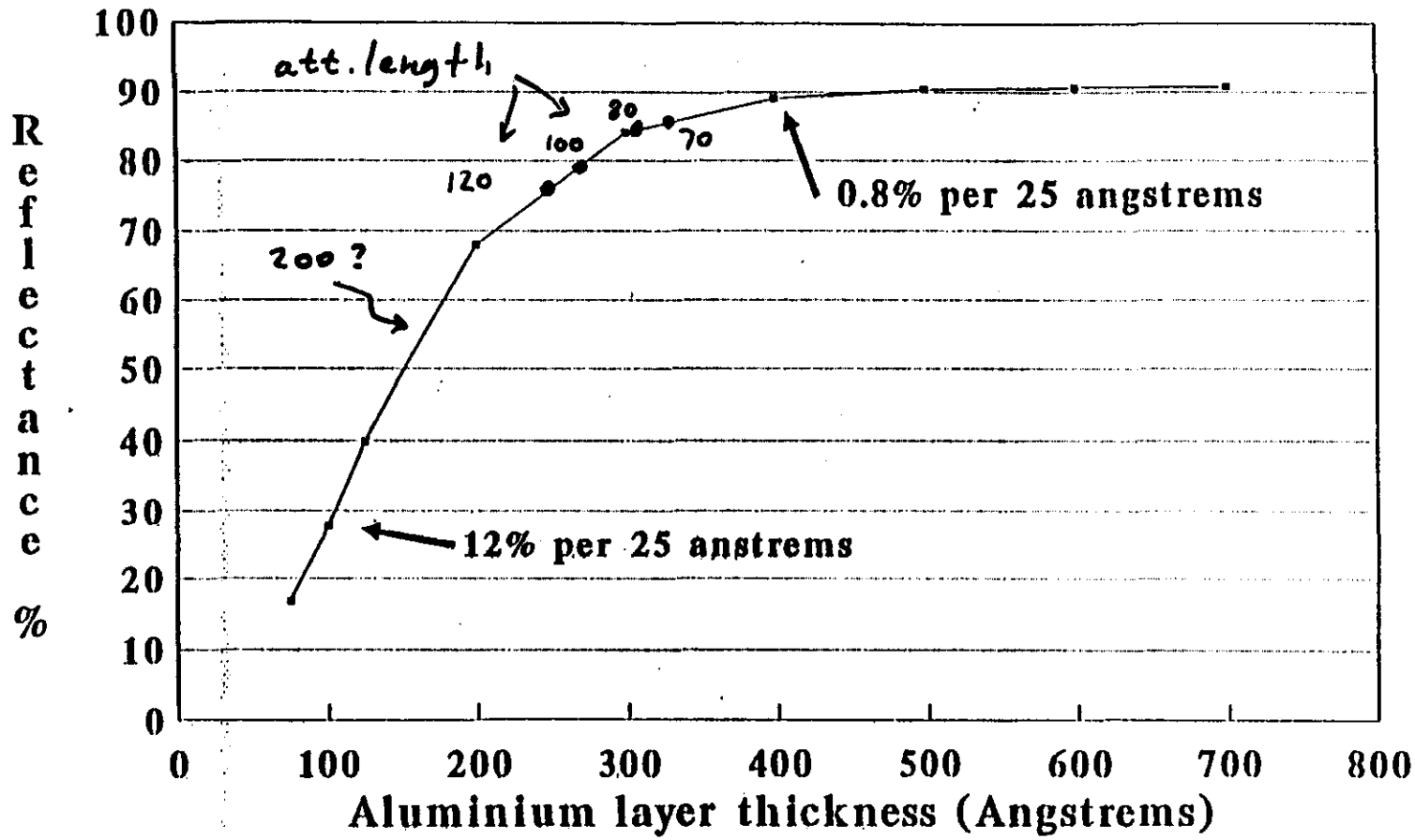


Fig 1-7 (b)

Reflectance of Al vs thickness

at 220 nm for BaF_2 composite coating
1000 Å MgF_2 + Al layer (in Angstrems)

expected thickness reproducibility +/- 25 angstrems



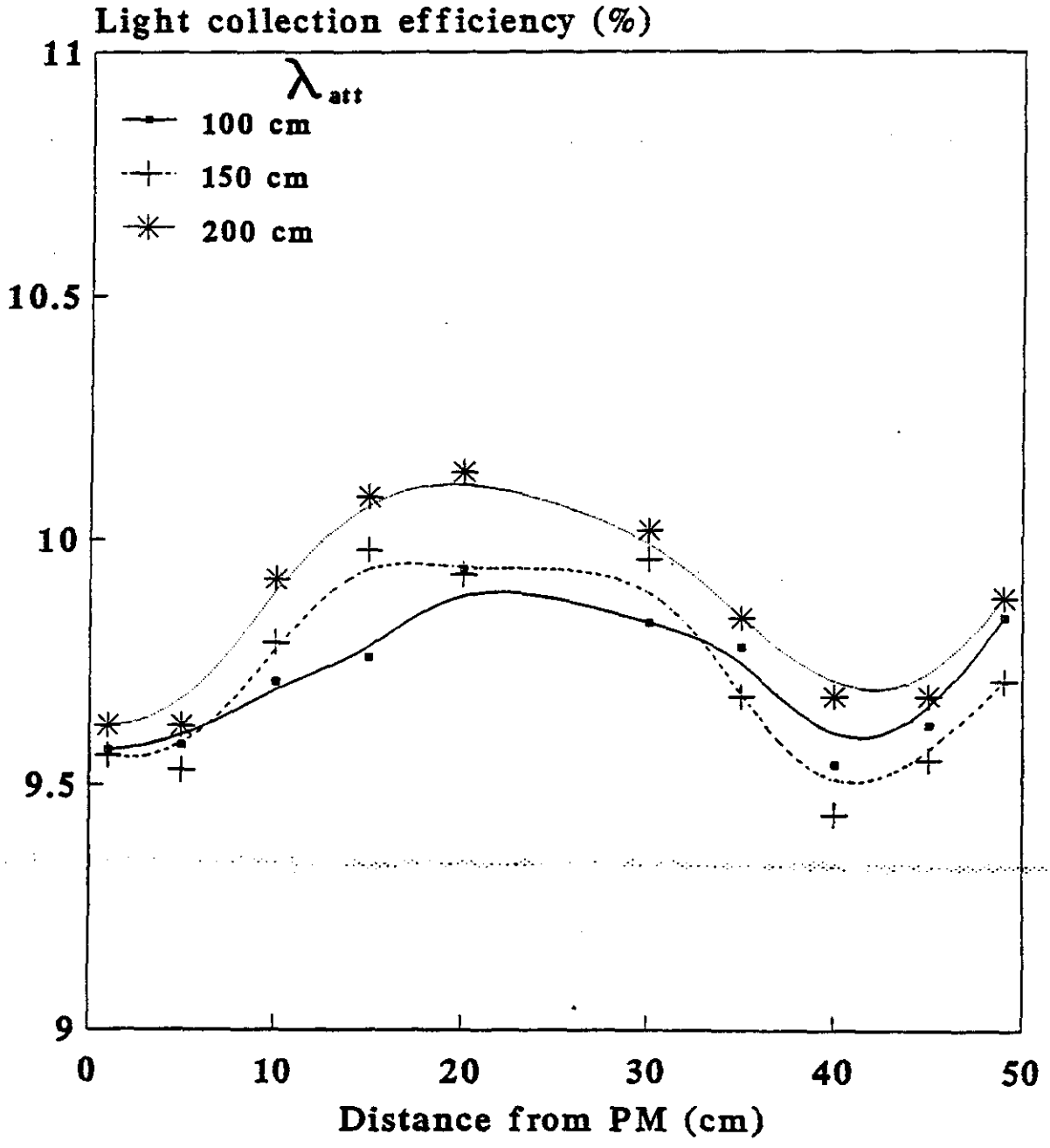
```
**********************************************
All uniform crystals, matrix 5 x 5:
  20 GeV:     0.272+- 0.007
  50 GeV:     0.230+- 0.006
 100 GeV:     0.220+- 0.004
 200 GeV:     0.249+- 0.011

**********************************************
Nonuniformity for LAMBDA = 200 cm, matrix 5 x 5:
  20 GeV:     0.530+- 0.015
  50 GeV:     0.394+- 0.011
 100 GeV:     0.346+- 0.010
 200 GeV:     0.264+- 0.012

**********************************************
Nonuniformity for LAMBDA = 150 cm, matrix 5 x 5:
  20 GeV:     0.433+- 0.012
  50 GeV:     0.312+- 0.009
 100 GeV:     0.260+- 0.008
 200 GeV:     0.204+- 0.025

**********************************************
Nonuniformity for LAMBDA = 100 cm, matrix 5 x 5:
  20 GeV:     0.616+- 0.017
  50 GeV:     0.464+- 0.013
 100 GeV:     0.407+- 0.014
 200 GeV:     0.304+- 0.013

**********************************************
Nonuniformity for LAMBDA = 78 cm, matrix 5 x 5:
  20 GeV:     0.268+- 0.006
  50 GeV:     0.240+- 0.007
 100 GeV:     0.221+- 0.006
 200 GeV:     0.243+- 0.011

**********************************************
Nonuniformity for LAMBDA = 76 cm, matrix 5 x 5:
  20 GeV:     0.277+- 0.008
  50 GeV:     0.212+- 0.004
 100 GeV:     0.199+- 0.005
 200 GeV:     0.198+- 0.007
```

absorbing mask

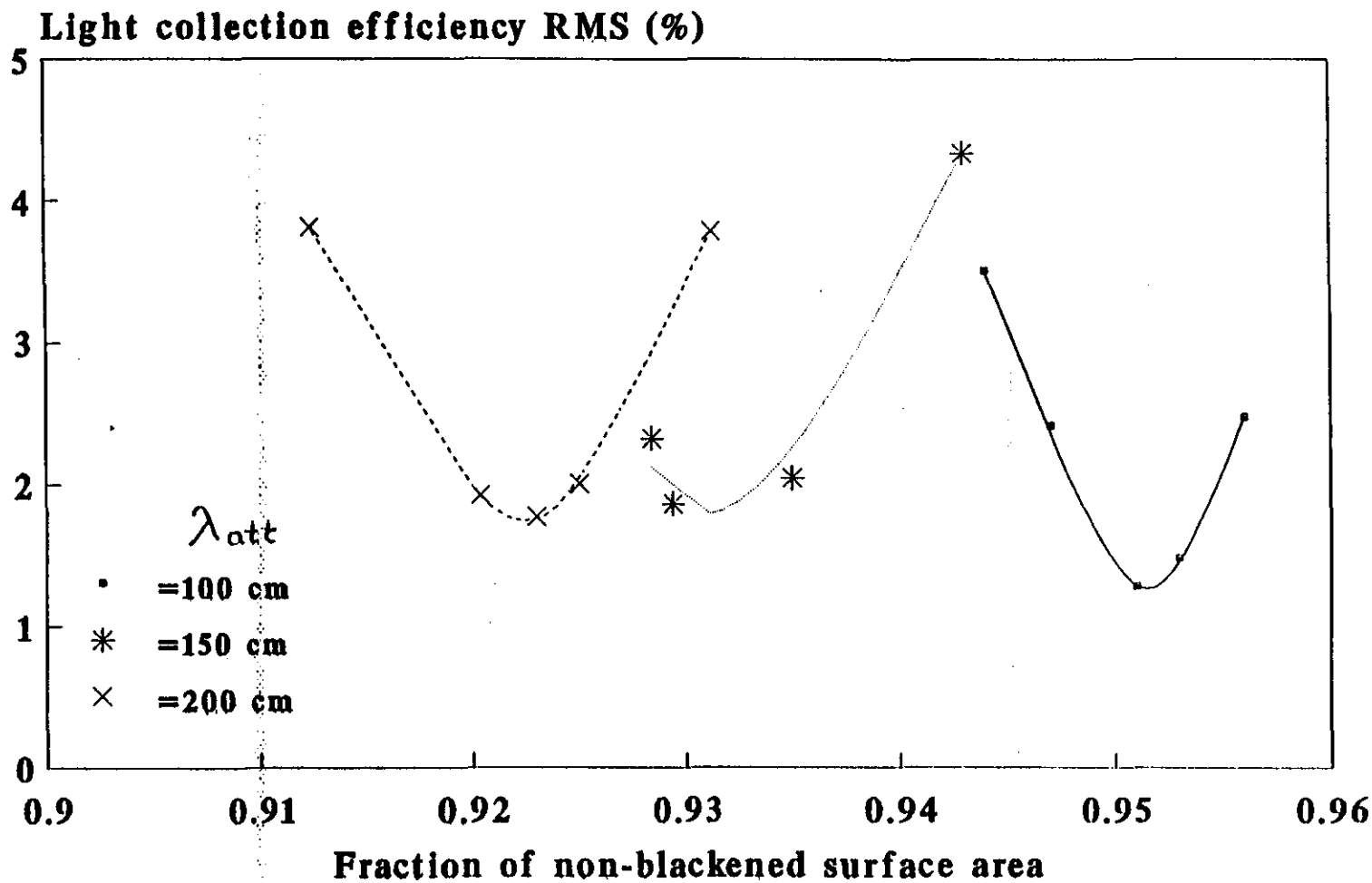
SiO_2

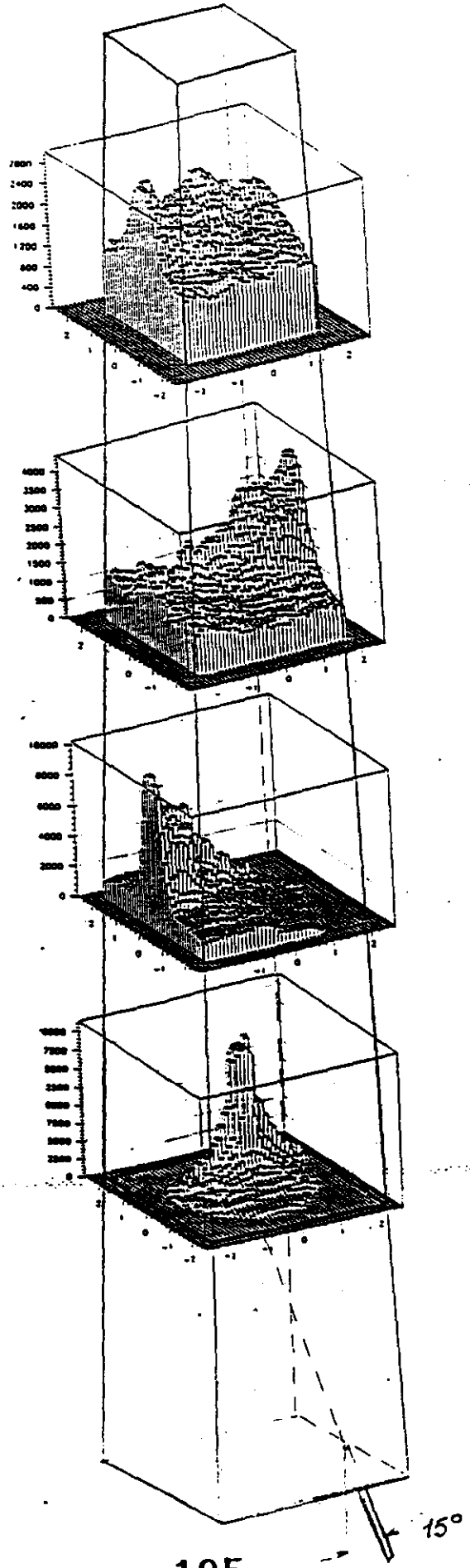
$MgF_2 + Al$

Uniformity for different λ_{att}
Polished surface



Optimization of surface coating
Polished surface

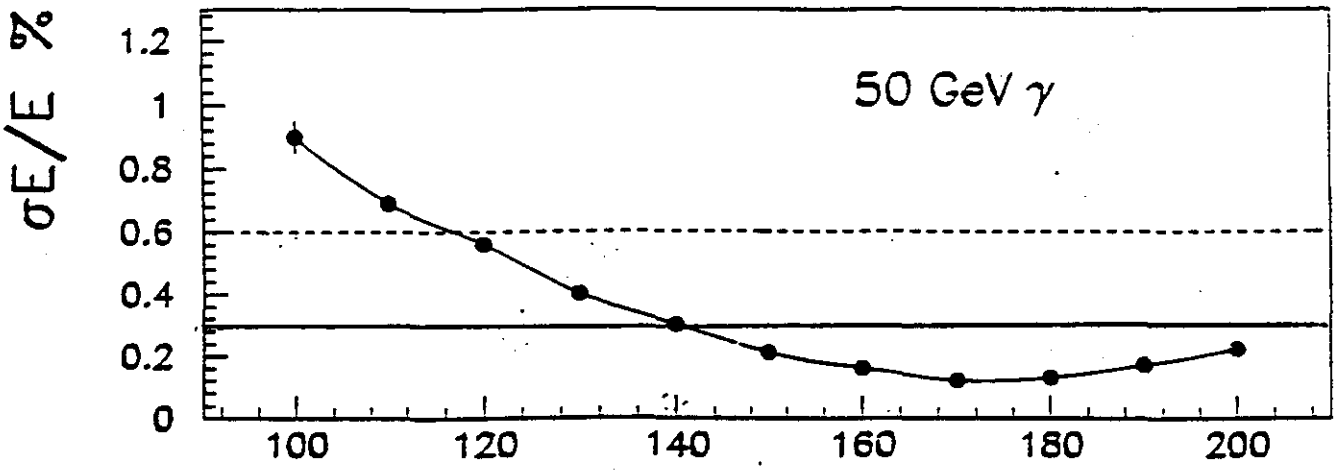



15°

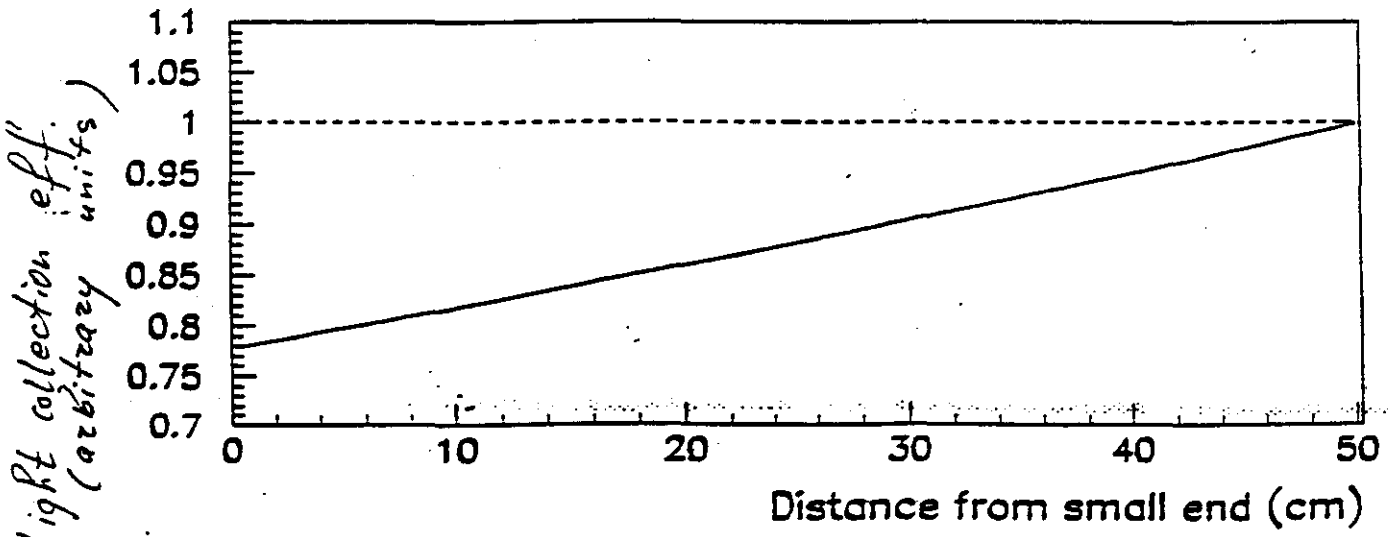
Radiation damage of all crystals

SCENARIO — all crystals were NOT preradiated

and were uniform with λ=200cm



Attenuation length(cm) after irradiation



Nonuniformity for λ=100cm (at saturation)

Fig 2-3

```
**********************************************
All uniform crystals
Pure signals (without leakage subtraction)
 50GeV     0.236+- 0.005    chi2 =   1.6885
100GeV     0.226+- 0.005    chi2 =   2.7321
200GeV     0.250+- 0.010    chi2 =   2.1566
```

uniform resolut...

```
**********************************************
Pure signals (without leakage subtraction):
At 200 cm (optimized)
 50GeV     0.283+- 0.008    chi2 =   1.1463
100GeV     0.250+- 0.008    chi2 =   1.8367
200GeV     0.221+- 0.009    chi2 =   1.1242

Transition from 200 cm to 150 cm, max shower at 150 cm
 50GeV     0.420+- 0.012    chi2 =   1.3091
100GeV     0.386+- 0.012    chi2 =   1.6577
200GeV     0.306+- 0.023    chi2 =   0.9783

At 150 cm (were optimized for 200 cm)
 50GeV     0.663+- 0.021    chi2 =   2.9053
100GeV     0.589+- 0.017    chi2 =   2.3146
200GeV     0.500+- 0.022    chi2 =   1.2756
```

Tarkovsky's curves

```
**********************************************

**********************************************
Pure signals (without leakage subtraction)
At 200 cm (assuming otimized to constant level)
 50GeV     0.234+- 0.005    chi2 =   1.6813
100GeV     0.226+- 0.005    chi2 =   3.1587
200GeV     0.249+- 0.010    chi2 =   2.3210

Transition from 200 cm to 150 cm, max shower at 150 cm
 50GeV     0.230+- 0.005    chi2 =   1.0190
100GeV     0.213+- 0.005    chi2 =   1.3703
200GeV     0.189+- 0.029    chi2 =   1.4832

At 150 cm (were optimized for 200 cm)
 50GeV     0.449+- 0.012    chi2 =   1.9911
100GeV     0.389+- 0.011    chi2 =   1.6223
200GeV     0.326+- 0.013    chi2 =   1.1682
```

assuming perfect coating at LAL = 200 cm

```
 50GeV      NEVENT   =   943
100GeV      NEVENT   =   943
200GeV      NEVENT   =   476
```

Expected dose rates for BaF_2 in GEM Detector at $L = 10^{33}\ cm^{-2}s^{-1}$

(rough estimate)

1) By ionizing particles at shower maximum
(~ 10–15 cm inside the BaF_2)
(similar to Co^{60} damage)

$\eta = 0 \quad \theta = 90° \quad \sim 50$ KRad / year
$\eta = 1 \quad \theta = 40° \quad \sim 100$ KRad / year
$\eta = 2.5 \quad \theta = 9° \quad \sim 1$ MRad / year

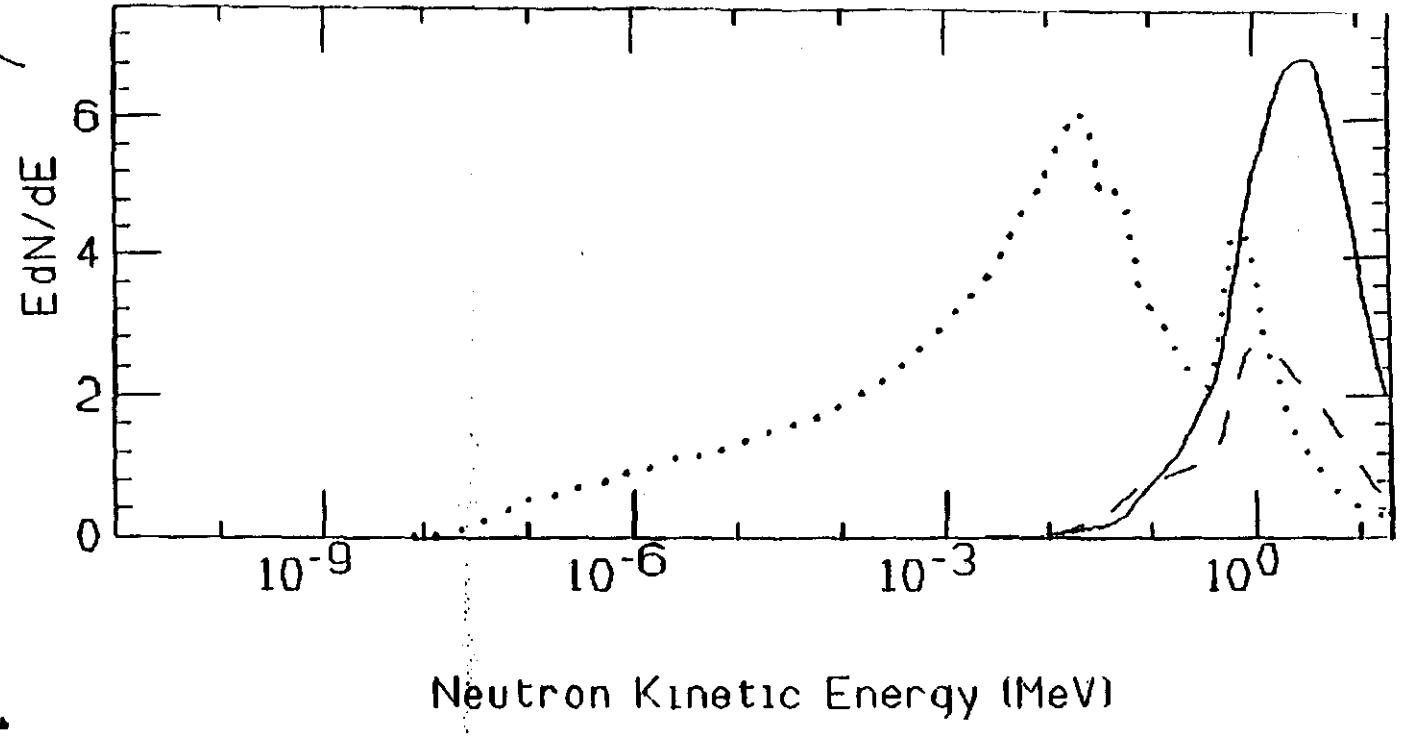
2) By neutrons with energy ~ 1 MeV

$\eta = 0 \quad \theta = 90° \quad \sim 5 \cdot 10^{12}\ n/cm^2/year$
$\eta = 1 \quad \theta = 40° \quad \sim 10^{13}\ n/cm^2/year$
$\eta = 2.5 \quad \theta = 9° \quad \sim 10^{14}\ n/cm^2/year$

3) Number of spallations
can be estimated on the request of the Panel

(3)

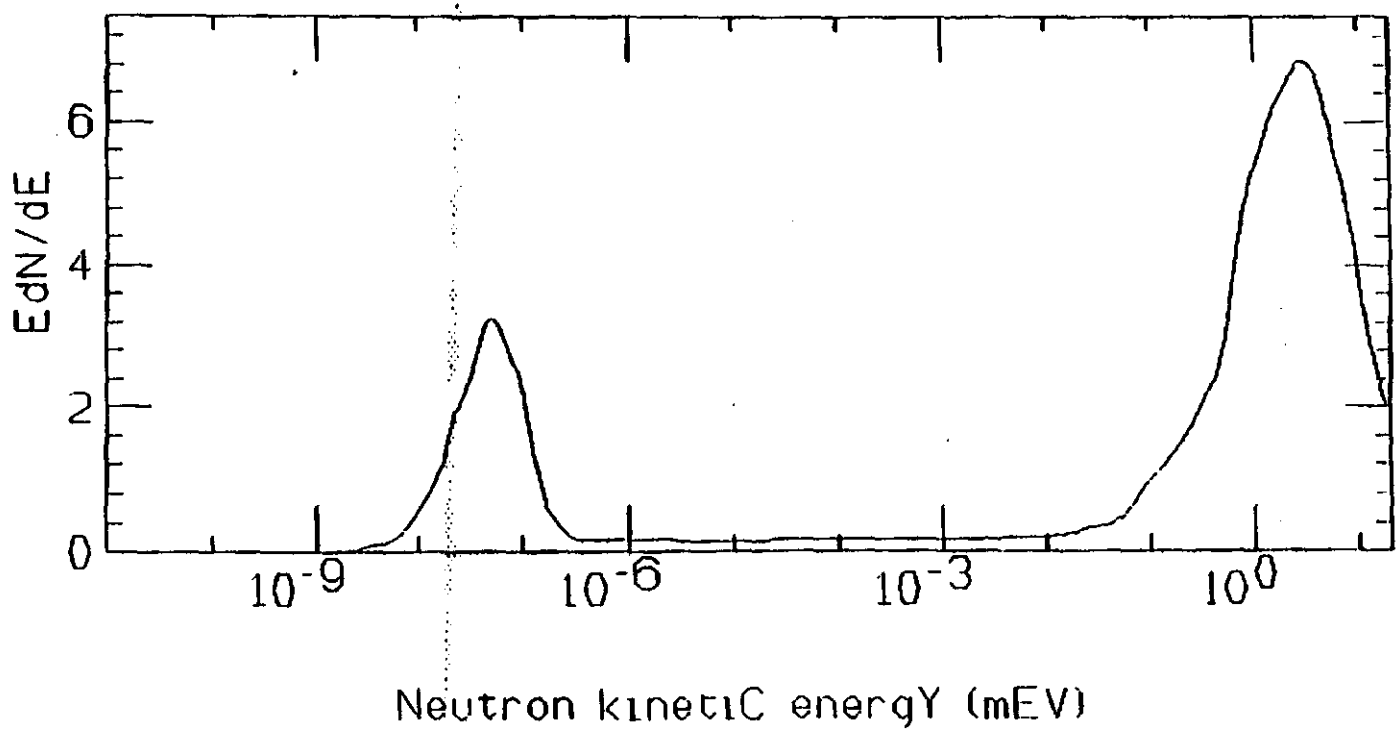
arbitrary scaling



— SINGLE CRYSTAL IN 800 MeV p beam 3cm x 3cm x 25cm

--- array of 25 crystals in 800 MeV p beam

..... BaF in GEM EM sections, DTUJET event generator



SINGLE crystal in 800 MeV p beam surrounded by water

L. Waters
LANL
Aug 31, 92

Questions to the Expert Group

- How LAL (light attenuation length) achieved after irradiation + UVLA depends on the quality of the crystals (impurities, growing process, chemical environment etc.) ?
- If such dependance is established, is it possible to control LAL after UVLA to the level say 180 ± 20 cm (precise values to be established) by production and material purity tolerances ?
- Can the requirements for material/crystal quality be relaxed if UVLA involved ?
- Will the achieved LAL level be the same for γ, p, n irradiation ?
- How stable is LAL if UVLA involved ?
  Is it saturated with dose ?
  Is it self-annealed with time ?
- Will the scheme Preirradiation-PreUVannealing work ?