

# 50 YEARS CRYSTAL GROWTH TECHNOLOGY

Hans J. Scheel

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Thanks, Thanks, Thanks

# Achievements I

- 1. First crystals of organic pigment dye quinacridone (Chinacridon), condition for structural research (1966).**
- 2. Explanation of the formation of “Pyroceram” glass ceramics by phase separation causing nucleation and bulk crystallization, with G. Bayer, O.W. Flörke and W. Hoffmann (1966).**
- 3. First large crystals of ferromagnetic semiconductor  $\text{NaCrS}_2$  from  $\text{Na}_2\text{S}_x$  solvent (flux) used also for growth of many other sulfides like  $\text{NaInS}_2$ ,  $\text{KCrS}_2$ ,  $\text{CdS}$ ,  $\text{ZnS}$ ,  $\text{PbS}$ ,  $\text{FeS}_2$ ,  $\text{CoS}_2$ ,  $\text{NiS}_2$ ,  $\text{MnS}$  etc. (1974).**
- 4. Forced convection for nucleation control and fast stable growth rates from high-temperature solutions by Accelerated Crucible Rotation Technique ACRT (1971,[1]). Hydrodynamics with E.O.Schulz-DuBois. Numerical simulation by Mihelcic et al., Kakimoto et al. and Derby et al.**
- 5. Evaluation of maximum stable growth rates in flux growth for inclusion-free crystals (with D. Elwell 1972, [1]).**
- 6. Ultra-sensitive temperature sensor based on Pt6 versus Pt30 thermopyle with C.H. West (1973).**
- 7. Slider-free LPE process for superlattices of p-n-GaAs (1977) and transition to faceting: atomically flat surfaces (1980) proven by Nomarski and by scanning tunneling microscopy (with G. Binnig and H. Rohrer), theory with A. Chernov (1995).**

## Achievements II

8. “Inherent” crystal growth problem of striations solved by ACRT and optimized T-control for flux growth of striation-free  $\text{KTa}_{1-x}\text{Nb}_x\text{O}_3$  (KTN) solid solutions (with D. Rytz 1982), theory with R.H. Swendsen (2001), [1].
9. Flame-fusion (Verneuil) growth of  $\text{SrTiO}_3$  with J. G. Bednorz (1977).
10. Growth of dislocation-free  $\text{SrTiO}_3$  crystals (with J. Hutton and R.J. Nelmes 1981).
11. Distribution coefficient  $k=1$  achieved in growth from high-temperature solutions (with R.H.Swendsen 2001).
12. First growth of colorless Anatase ( $\text{TiO}_2$ ) crystals by chemical vapor transport (with M. Graetzel et al. 1996).
13. First free crystals of high-temperature superconductor  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  and thick YBCO crystals grown from high-temperature solutions (with F. Licci 1988, W. Sadowski 1989, [1]).
14. Leading-edge growth mechanism discovered on thin YBCO plates explaining growth of majority of thin plates in unstable growth regime (with Ph. Niedermann 1989, confirmed by H. Müller-Krumbhaar).
15. LPE of YBCO and NdBCO (with C. Klemenz 1992-1996, parallel with P. Görnert in Jena).
16. LPE of GaN (with C. Klemenz 2000).
17. Definition of 8 epitaxial growth modes (1997, in [1] and [2] 2007).
  - Construction of versatile Verneuil furnace for growth-rate measurements;
  - of ultra-pure glovebox system with  $\text{O}_2$  and  $\text{H}_2\text{O}$  below detection limit;
  - of Czochralski model with four visualization methods.

## Videos in Section „Crystal Growth“ of Website [www.hans-scheel.ch](http://www.hans-scheel.ch)

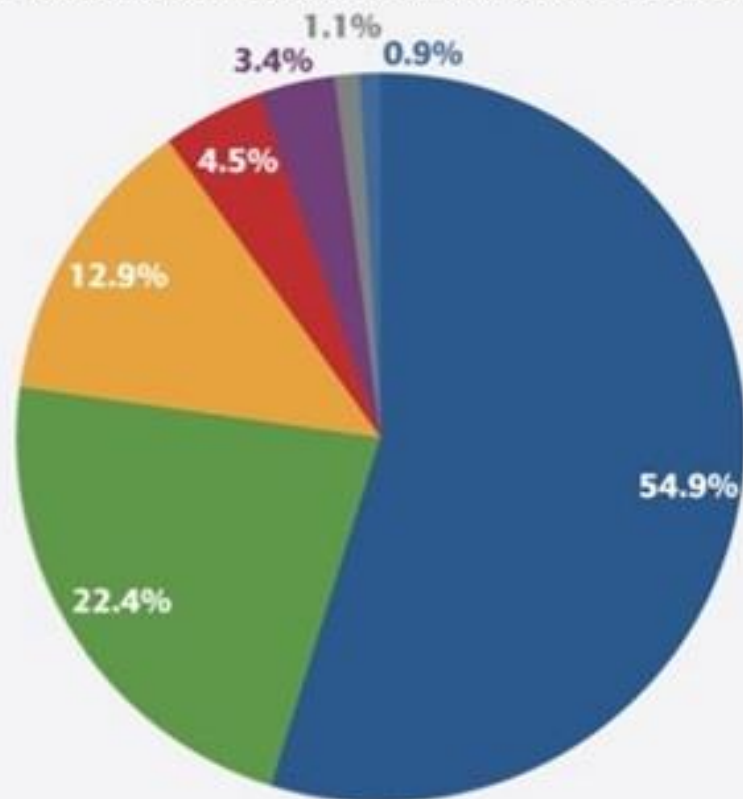
- Acknowledgments & Thanks
- My Early 25 Years
- Organic Pigment Dyes
- Pyroceram-type Glasses
- Crystal Growth of NaCrS<sub>2</sub>
- Zero or Forced Convection
- ACRT
- \* Striation Problem solved
- \* Strontium Titanate
- \* Slider-free LPE +Super-Glovebox
- \* Czochalski Flow
- \* High-Tc Superconductors
- \* My New Projects
- \* My New Family



SZ-45846

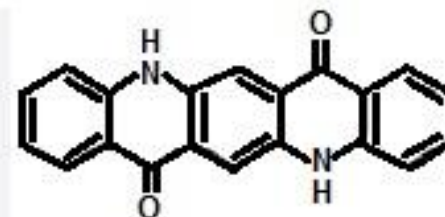
**COATINGS WORLD:** With an overall value of \$4.76 billion, the market for high performance pigments is poised for steady growth worldwide. Quinacridone 2016 178.844 tons.

1960: CIBA, Farbwerke Hoechst, DuPont, now Clariant India & China, AkzoNobel



- Coatings
- Plastics
- Inks
- Cosmetics
- Textiles
- Electronics
- Non-impact printing

**High-Performance Pigment Market by Segment**



MP dec. ~400°C

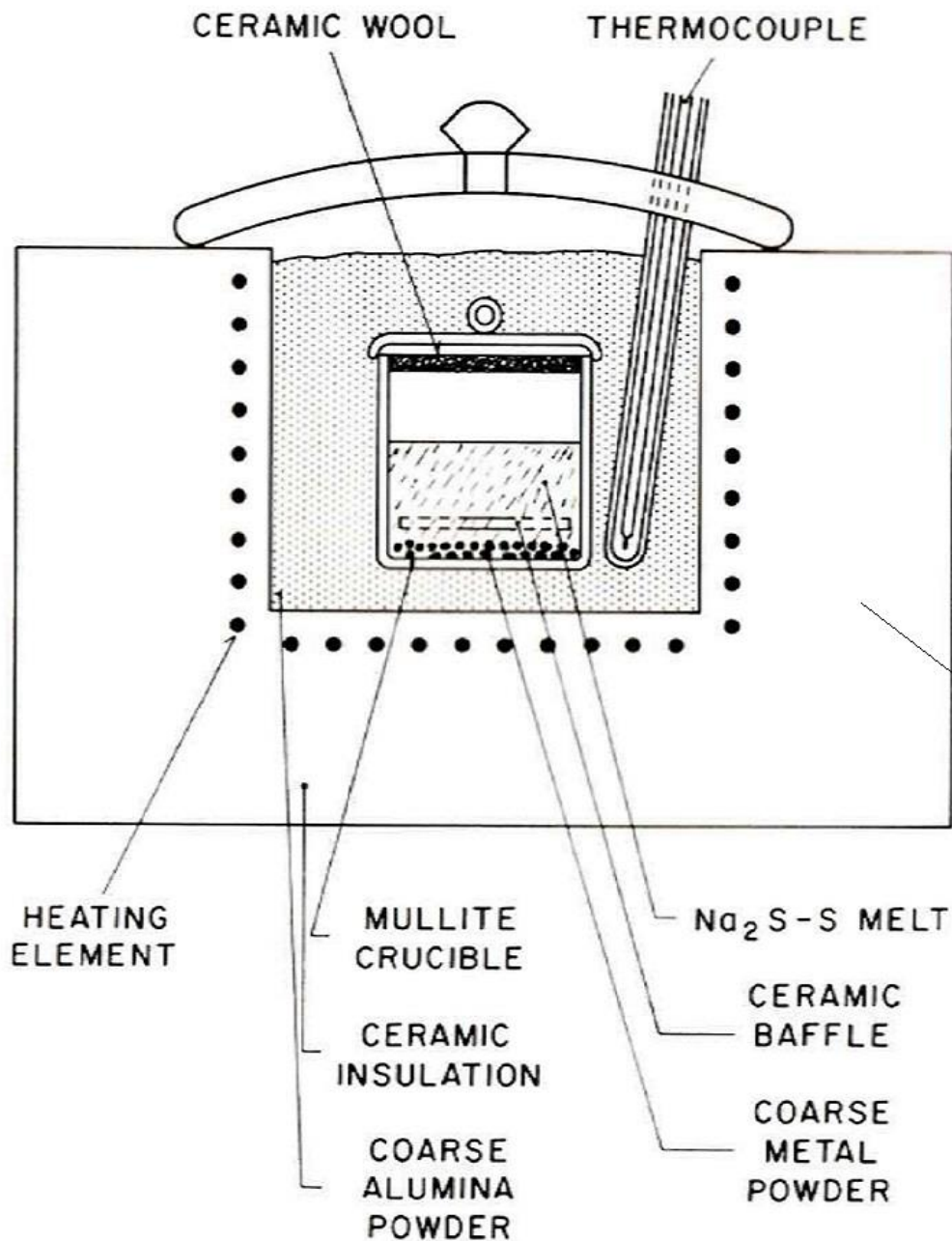
Unsoluble



**Growth by Sublimation**

H. Koyama, F. Laves, H.J. Scheel:  
Kristallstrukturen organischer  
Pigmentfarbstoffe I:  
g-Chinacridon C<sub>20</sub>H<sub>12</sub>O<sub>2</sub>N<sub>2</sub>,  
*Naturwiss.* 53(1966)700.

K. Ogawa, F. Laves, H.J. Scheel:  
II: 4,4'-Diamino-1,1'-  
Dianthrachinonyl C<sub>28</sub>H<sub>16</sub>N<sub>2</sub>O<sub>4</sub>,  
*Naturwiss.* 53 (1966)700-701.



## Growth of $\text{NaCrS}_2$ from $\text{Na}_2\text{CO}_3$ - $\text{K}_2\text{CO}_3$ melts:

R. Schneider:

J. Prakt. Chem. 8(1873)38, 56(1897)415

S. Haussühl, M. Schieber: unpublished

## Growth of $\text{NaCrS}_2$ from $\text{Na}_2\text{S}_x$ -Melts: H.J. Scheel:

J. Crystal Growth 24/25(1974)669-673

See also in D. Elwell and H.J. Scheel:

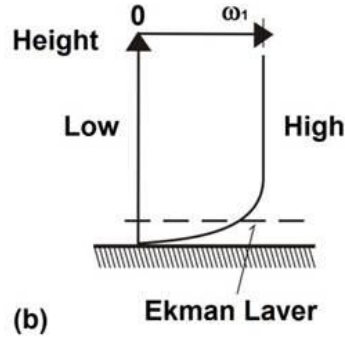
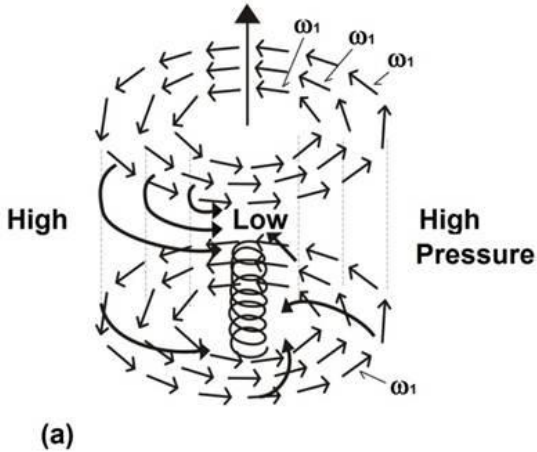
**Crystal Growth from High-Temperature Solutions**,  
Academic Press 1975, E-scan with Chapter 11 and  
2 Appendices in [www.hans-scheel.ch](http://www.hans-scheel.ch)

## Simon-Müller-Furnace

Fig. 1. Arrangement of crucible with alkali polysulfide melt in the muffle furnace.

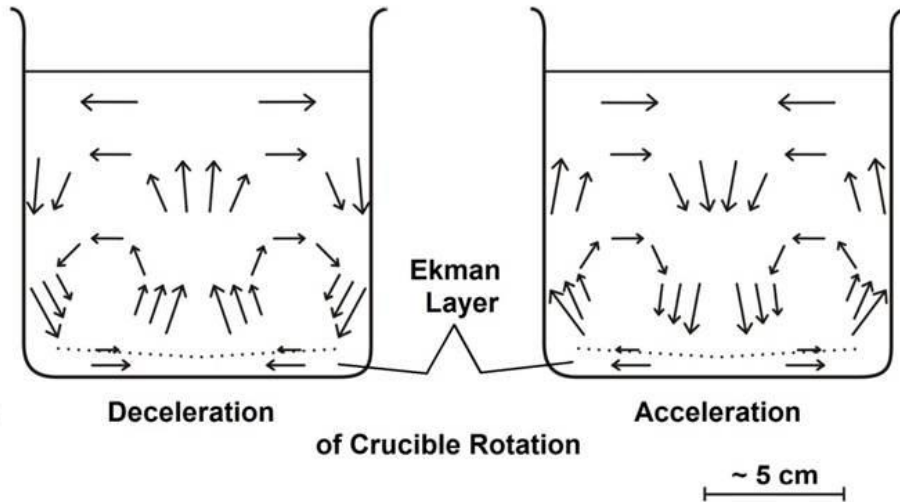
# Tornado

*Problem of H. Rohrer 1969: Large GdAlO<sub>3</sub> crystals*



Schematic View of a Tornado with Flow Profile (a) and Velocity Distribution in the Surface Friction (Ekman) Layer (b).

## Spiral-Shear Flow and Ekman-Layer Flow, Movie at ICCG Marseille 1972

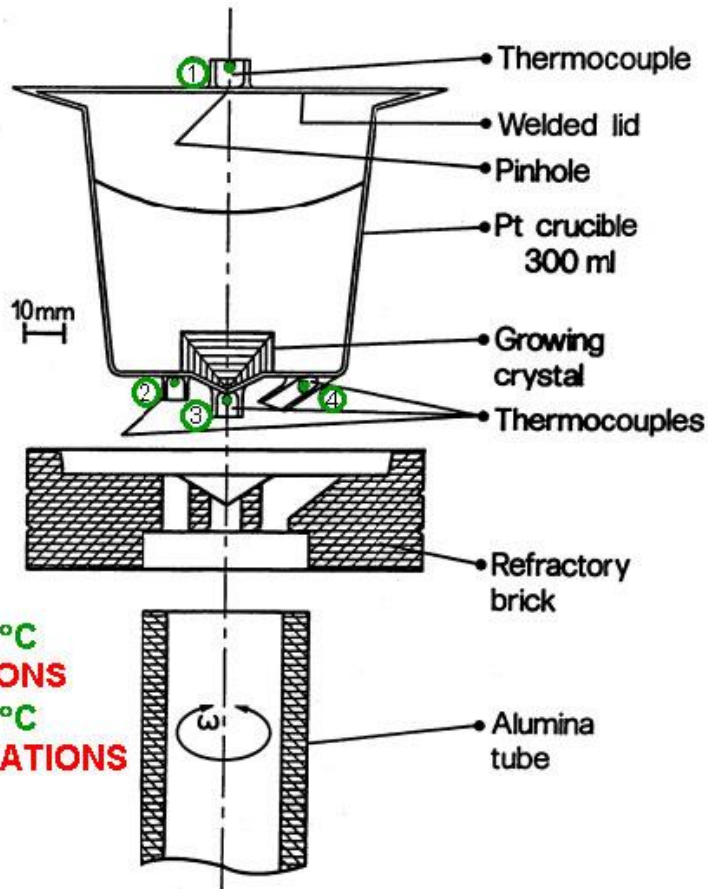
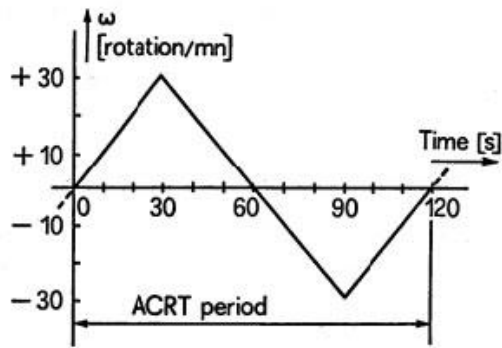


The Ekman Layer Flow occurs also in a circular Container with flat Bottom (c) when its Rotation is decelerated, and the opposite Flow upon Acceleration (d).

(d) Accelerated Crucible Rotation Technique (ACRT)  
H.J.Scheel, J. Crystal Growth 13/14(1972)560-565

## Accelerated Crucible Rotation Technique ACRT





$T_1 - T_d \approx 25^\circ\text{C}$   
 → STRIATIONS  
 $T_1 - T_d \approx 10^\circ\text{C}$   
 → NO STRIATIONS

- Theory & Film with Erich Schulz-DuBois 1971, IBM
- Computer Simulation & Film M. Mihelcic 1979  
KFA Jülich

### ACRT in Growth from High-Temperature Solutions

- GdAlO<sub>3</sub> & Solid Solutions, GdAlO<sub>3</sub>:Cr, LaAlO<sub>3</sub>, KTN, Magnetic Garnets, SrTiO<sub>3</sub>: H.J. Scheel, IBM Zurich
- Magnetic Garnets: W. Tolksdorf, Philips Hamburg
- Magnetic Garnets: P. Görnert, Jena/DDR
- Emerald: G. Bukin, Novosibirsk
- Pb(Fe<sub>0.5</sub>Nb<sub>0.5</sub>)O<sub>3</sub>, Pb(Mn<sub>0.5</sub>Nb<sub>0.5</sub>)O<sub>3</sub> with Hans Schmid et al. and P. Tissot.

### ACRT in Bridgman Growth (> flat growth surface)

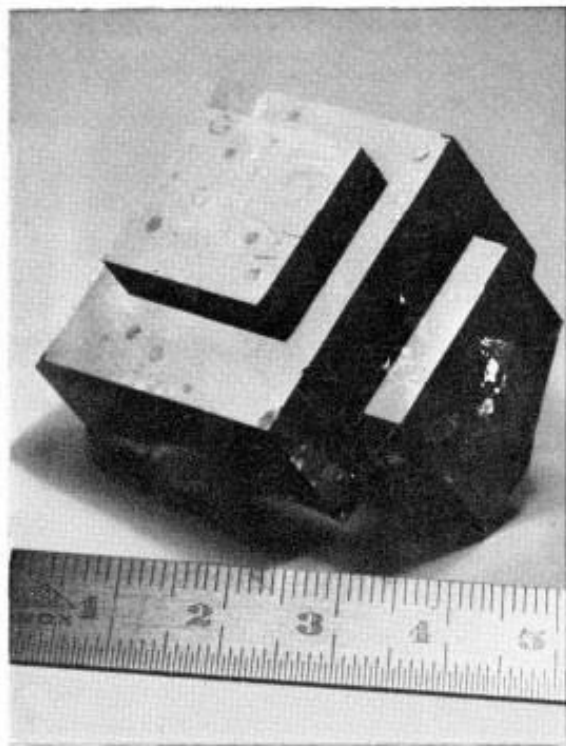
- Halogenides: A. Horowitz, Israel
- CdTe/HgTe Solid Solutions: P. Capper, Millbrook Southampton UK
- III-V Solid Solutions: P. Dutta, Rensselaer Polytechnic Troy N.Y.

### ACRT in Growth from Vapor

- CdS: H.J. Scheel (unpublished)

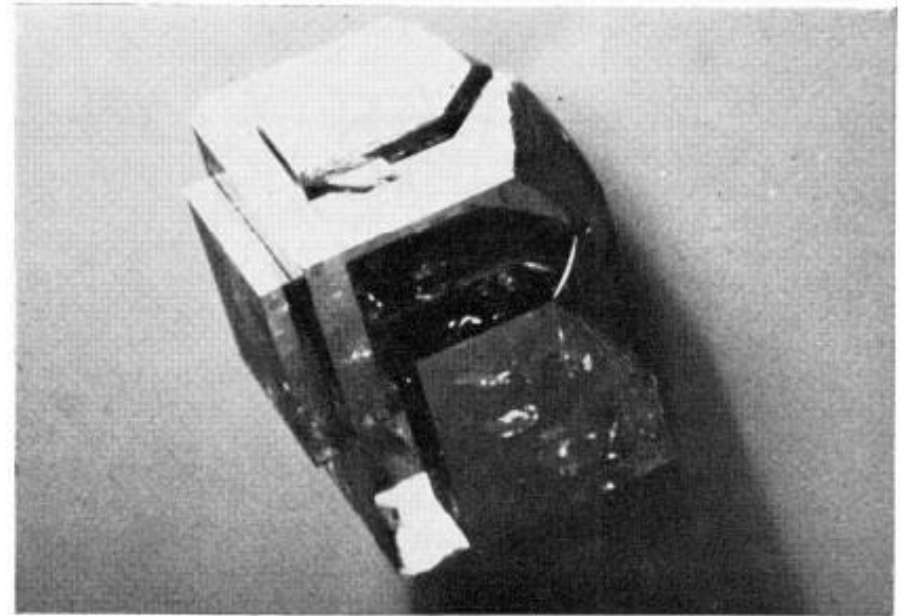
List not complete

Temperature Measurement  
 at Rotating Crucible at high Temperature



(a)

ACRT  
 $\text{GdAlO}_3$   
Perovskite  
 $\text{Gd}_{1-x}\text{La}_x\text{AlO}_3$   
 $\text{Gd}_{1-x}\text{Y}_x\text{AlO}_3$   
 $\text{Y}_3\text{Fe}_{5-x}\text{Ga}_x\text{O}_{12}$



(b)

- H.J. Scheel: Accelerated Crucible Rotation: A Novel Stirring Technique in High-Temperature Solution Growth. *J. Crystal Growth* **13/14** (1972) 560-565.
- H. Rohrer and H.J. Scheel: Experimental Verification of Random-Field Critical and Multicritical Behavior. *Physical Review Letters* **44** (1980) No.13, 876-879.
- H.J. Scheel and R.H. Swendsen: Evaluation of Experimental Parameters for Growth of Homogeneous Solid Solutions. *J. Crystal Growth* **233** (2001) 609-617.
- H.J. Scheel: Theoretical and Technological Solutions of the Striation Problem. *J. Crystal Growth* **287** (2006) 214-223.

Table 2

Characteristics of various growth experiments of  $KTa_{1-x}Nb_xO_3$  mixed crystals

## 20 KTN Papers: Growth Conditions

472

D. Rytz, H.J. Scheel / Growth of  $KTa_{1-x}Nb_xO_3$  ( $0 < x \leq 0.04$ ) solid solutions

Bell

Refs.	Composition range	Growth method	Thermal regulation	Cooling interval	Cooling rate ( $^{\circ}C h^{-1}$ )	Mass of melt (g)	Composition of melt (mole% $K_2CO_3$ )	Additives	Loss ( $g h^{-1}$ )
[19]	$0.2 \leq x \leq 1.0$	Kyropoulos	$\pm 0.1^{\circ}C$	$\sim 15^{\circ}C$	0.1–0.5	20	50	None	?
[29]	0.35	TSSG	?	?	0.1	1300	50–52	$SnO_2$ (0.1 mole%)	?
[30]	0.35	TSSG and "floating crystal"	?	?	?	350	53–60	None	0.06–0.2
[31]	0.35	Hydrothermal	?	–	–	–	Excess KOH	–	–
[32]	0.35	TSSG	?	?	?	32000	50	CaO, PbO, ...	0.2
[33]	0.35	Hydrothermal	?	–	–	10	Excess KOH	$SnO_2$ (1 wt%)	–
[34]	$0.30 \leq x \leq 0.39$	Pfann technique	$\pm 0.5^{\circ}C$	–	–	1400	65	$SnO_2$ (0.5 wt%)	?
[35]	$0.40 \leq x \leq 0.55$	TSSG and spontaneous nucl.	?	?	2–6	600	70	None	?
[36]	$0.34 \leq x \leq 0.40$	TSSG	?	?	?	1000	52–65	$SnO_2$ (0.1 mole%)	?
[37]	0.25	TSSG	?	?	?	800	52	None	?
[20, see also ref. [8]	$0.05 \leq x \leq 0.60$	TSSG	?	?	0.5	?	60	$SnO_2$ (10 ppm)	?
[38], see also ref. [39]	Various	TSSG	?	?	?	800	$\geq 50$	–	?
[28]	0.38	Mass transfer	$\pm 0.1^{\circ}C$	–	–	400	55	None	?
[40]	0.35	Mass transfer	?	–	–	1400	53.5	$SnO_2$ (0.1 mole%)	?
[41]	0.35	Mass transfer	$\pm 0.1^{\circ}C$	–	–	400	55	None	Considerable
[22], see also refs. [24,42–44]	$0 \leq x \leq 0.10$	Spontaneous nucl.	$\pm 2^{\circ}C$	$500^{\circ}C$	5	20	55–60	CuO, $Fe_2O_3, \dots$	?
[45]	0.28 and 0.40	Mass transfer	?	–	–	?	–	None	?
[46]	0.30	TSSG	?	?	?	?	?	–	?
Present work	$0 < x < 0.04$	Slow cooling	$\pm 0.1^{\circ}C$	$\sim 40^{\circ}C$	0.15	1100	60	None	0.1

R + S

Table 2 (continued)

## KTN Papers: Growth Results

Refs.	Growth rate ( $\text{\AA s}^{-1}$ )	Size of resulting crystals ( $\text{mm}^3$ )	Developed faces	Colour	Characterization	Measured $\Delta x$ (local)	Calculated $\Delta x$ (total)	Striations	Other defects
[19]	350	$6.5 \times 6.5 \times 3.2$	(100)		Dielectric constant	0.03	0.10	?	
[29]	720	$15 \times 10 \times 10$	(100)	Colourless	Dielectric constant	0.002	0.02	Yes	
[30]	2800	$15 \times \varnothing 10$		Colourless	X-ray fluorescence	?	0.06	Yes	"Some" strain
[31]	?			Colourless	X-rays; microprobe	?	—	Yes	Exsolution patterns
[32]	360	$80 \times 80 \times 30$	(100) and minor (110)	Colourless	X-ray fluorescence	0.01	0.10	Yes	Bell
[33]	710	$5 \times 5 \times 5$	(100) and minor (111)			?	—	Yes	
[34]	850	$40 \times 40 \times 30$	(100)		Dielectric constant	0.01	—	Yes	
[35]	?	$8 \times \varnothing 15$ $5 \times 5 \times 2$		Pale yellow	X-rays; dielectric constant	?	0.04	?	Cracks
[36]	?	?		Colourless	Resistivity	?	?	?	
[37]	2000	$8 \times 8 \times 7$	(100)		Dielectric constant	0.01	0.01	?	
[20], see also ref. [8]	1400	1000–3000	(100)		Volumetric method	0.08	?	?	Large strain; grain boundaries
[38], see also ref. [39]	400–2800	2000	(100)			0.01	0.04	?	
[28]	220–420	1000	(100) and minor (110)	Colourless	Resistivity	?	—	?	
[40]	4000	$50 \times 50 \times 10$	(100)	Colourless		?		Yes	Inclusions
[41]	1200	$30 \times 30 \times 20$	(100) and minor (110)		Microprobe	0.04	—	Yes	
[22], see also refs. [24,42–44]	300	$10 \times 5 \times 5$	(100)	Yellow	Microprobe; density; dielectric constant; elastic step	0.003	0.25	Yes	
[45]	120	1000		Colourless	Dielectric constant; resistivity	?	—	?	Mosaic spread $0.01^\circ$
[46]	?	?		Blue	Resistivity	?	?	?	
Present work	100–400	$25 \times 25 \times 10$	(100)	Colourless	Microprobe; elastic step	$< 0.03$	0.06	Very faint	R + S

D. Ryz, H.J. Scheel / Growth of  $\text{KTa}_{1-x}\text{Nb}_x\text{O}_3$  ( $0 < x \leq 0.04$ ) solid solutions

PhD Thesis at ETH Lausanne IBM Zurich Research Laboratory

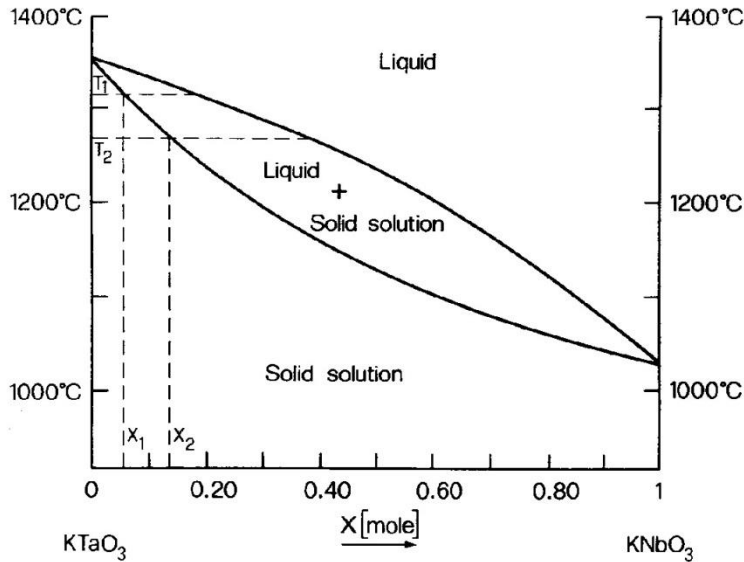


Fig. 2. Schematic solid-solution phase diagram (after ref. [5]). Growth starts at temperature  $T_1$  with an initial concentration  $x_1$ , and ends at temperature  $T_2$  with a final concentration  $x_2$ .

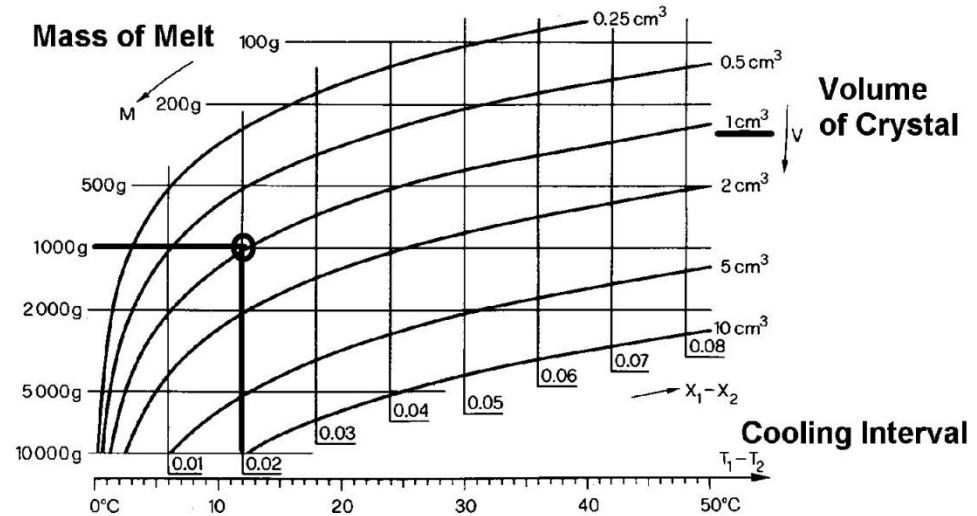


Fig. 3. Plot of crystal size  $V$  and inhomogeneity  $x_1 - x_2$  as a function of experimental parameters (mass of melt  $M$  and cooling interval  $T_1 - T_2$ ). A numerical example is detailed in the text.

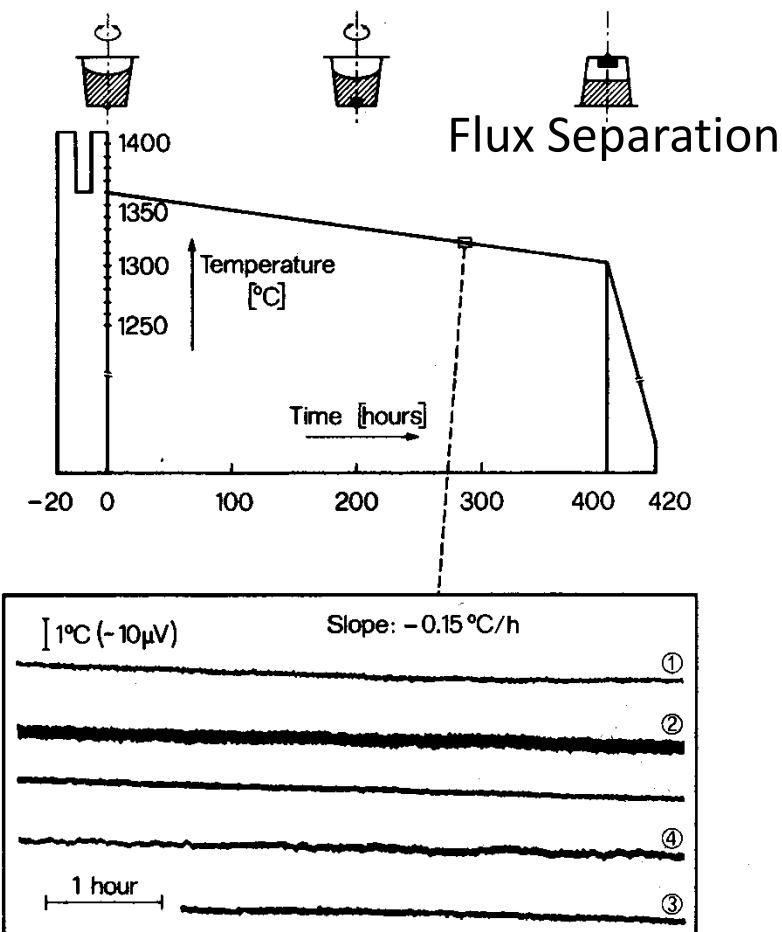


Fig. 7. Different steps of a growth experiment. A short interval during cooling is shown on a real temperature plot. The numbers correspond to the thermocouples of fig. 6. The unlabelled thermocouple was located at the back of the furnace.

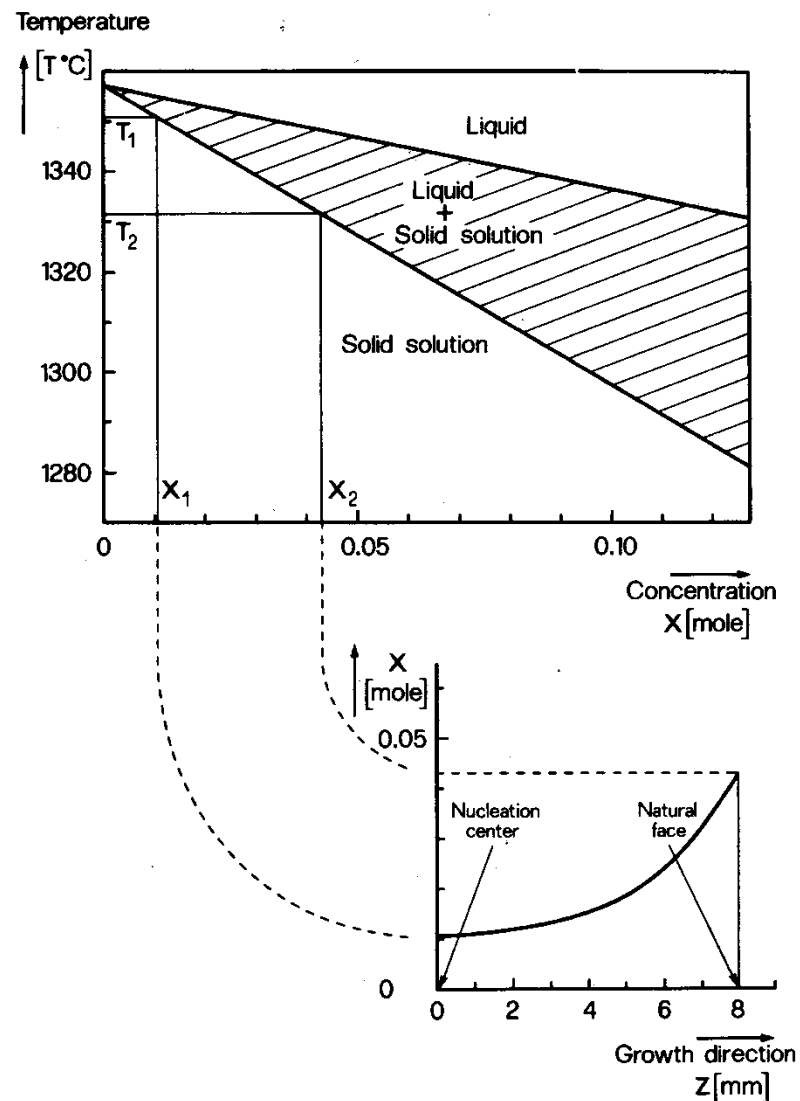


Fig. 4. Schematic phase diagram of  $\text{KTa}_{1-x}\text{Nb}_x\text{O}_3$  and spatial variation of the concentration  $x$  along the growth direction  $z$ . The inherent bulk concentration gradient induced by the slow-cooling method is clearly shown. (The numerical values  $T_1 - T_2 = 20\text{ }^{\circ}\text{C}$ ,  $x_1 - x_2 = 0.03$  and  $V \sim 8 \times 16 \times 16\text{ mm}^3$  correspond roughly to the numerical example detailed in the description of fig. 3.)

# Conditions for Growth of Striation-Free Crystals

1. Flat (smooth) Growth Surface
  2. Isothermal Growth Surface  $\leftarrow \Delta T/T < 10^{-5}$
  3. Homogeneous Melt or Solution  $\Delta n/n < 10^{-6}$
  4. Constant Growth Rate  $\Delta V/V < 10^{-5}$
- 

**When above conditions are established:**

Hydrodynamic Fluctuations are  
not harmful.

Forced Convection and ACRT  
can Assist to Homogenize the  
Melt or Solution.

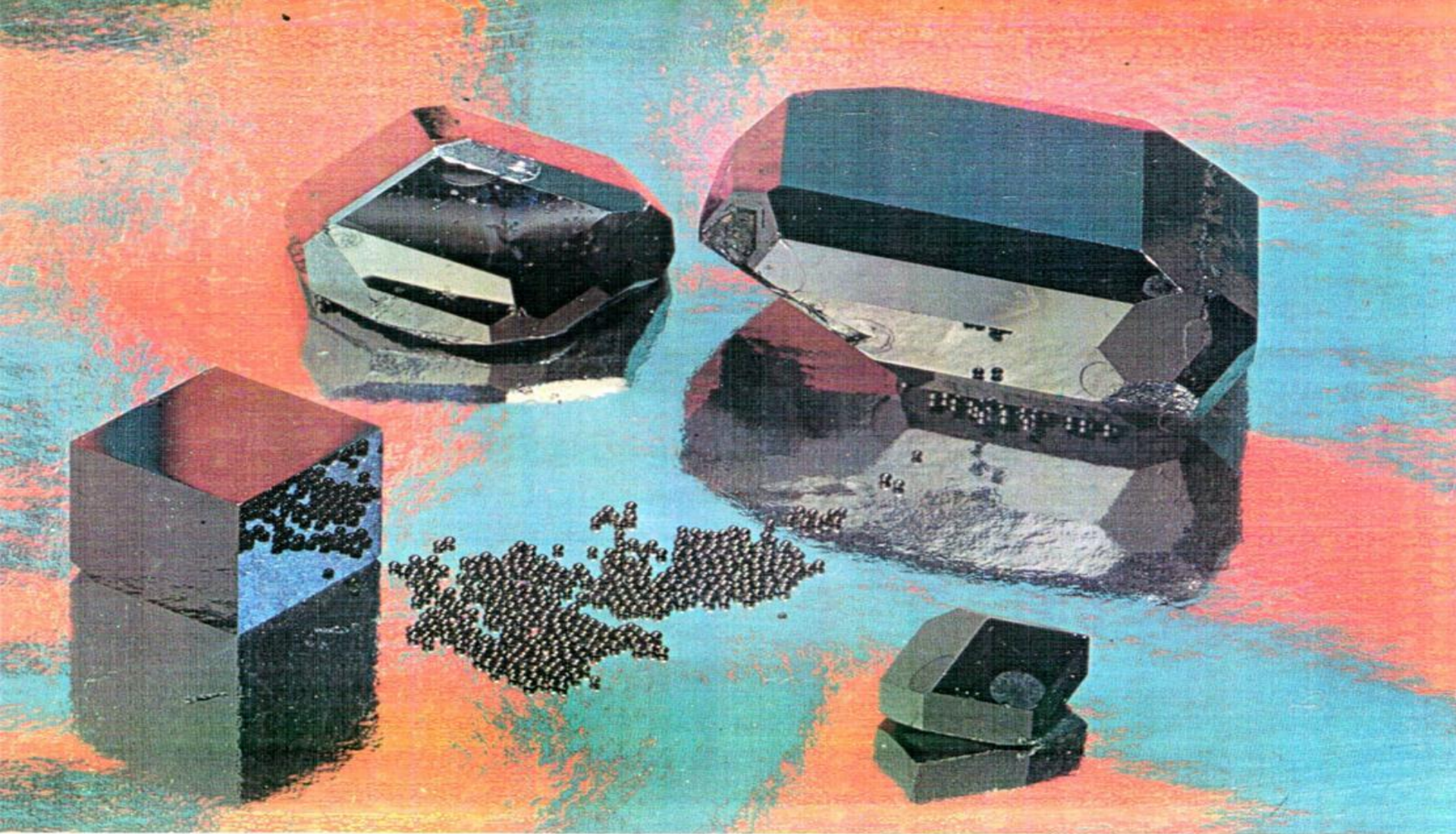
+ Precise Temperature Control.

J.A. Burton, R.C. Prim,  
W.P.Slichter: J. Chem. Phys.  
21(1953)1987-1991  
Keff for growth from melts

W. Van Erk: J. Crystal Growth  
57(1982)71-83  
Keff for growth from  
solutions

W. Nernst: Z. Phys. Chem.  
47(1904)52-55  
Diffusion-limited growth rate  
 $V = \sigma D / \rho \delta$

H.J. Scheel and R.H. Swendsen: Evaluation of Experimental Parameters for  
Growth of Homogeneous Solid Solutions. J. Crystal Growth 233(2001)609-617

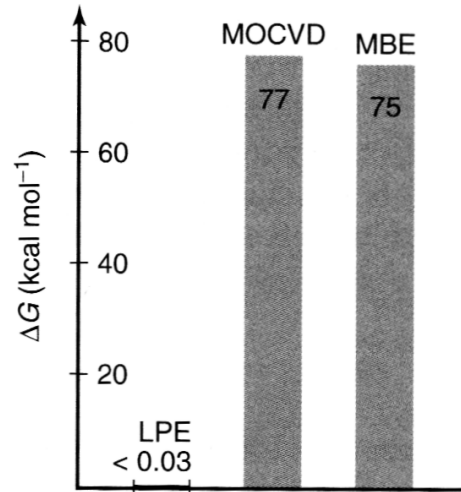


### **YIG Crystals ACRT-grown by Wolfgang Tolksdorf for Philipps Microwave Devices**

Homogeneity importance for magnetic, magneto-optic, ferroelectric, nonlinear-optic and photorefractive applications: Crystal Growth and Electro-optic Properties of Oxide Solid Solutions: H.J. Scheel and P. Günter, Chapter 12 in *Crystal Growth of Electronic Materials*, editor E. Kaldis, Elsevier 1985.



# Supersaturation in Growth from Vapor and in LPE



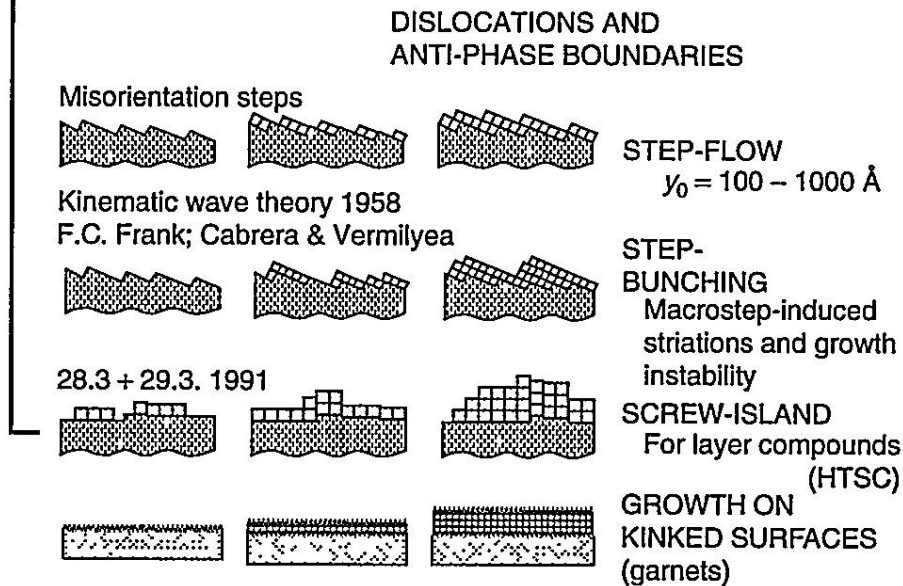
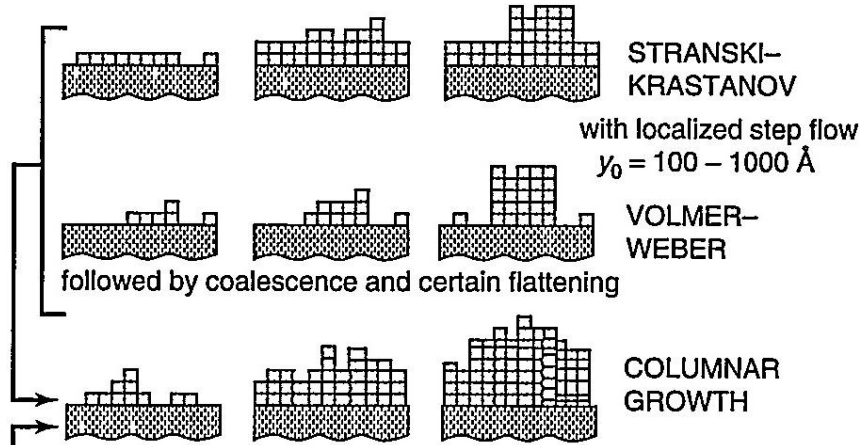
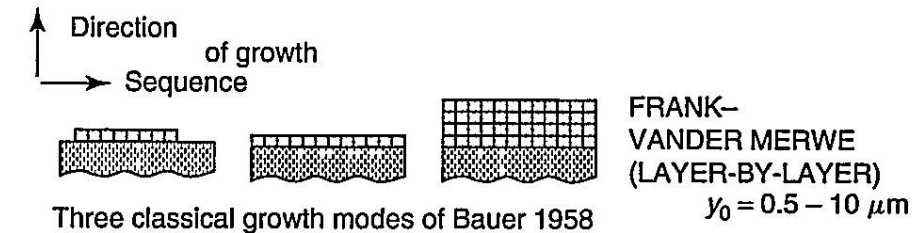
**G. Stringfellow  
1991**

Gibbs free energy differences between reactants and products (layers, crystals). The estimated thermodynamic driving forces for LPE ( $\Delta T < 6$  K), MOCVD (TMGa + arsine) and MBE (Ga + As<sub>4</sub>) of GaAs at 1000 K. (After Stringfellow, 1991) Reprinted from *J. Cryst. Growth*, **115**,

Supersaturation ratios for VPE and LPE derived from interstep distances  $y_0$  of GaAs and of the high-temperature superconductor YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7-x</sub> (YBCO)

	For GaAs		For YBCO	
	MBE, MOVPE	LPE	VPE, MOVPE	LPE
$y_0$	20–100 nm	6 μm	14–30 nm	6 μm (0.6–17 μm)
$r_S^*$	1.1–5.5 nm	300 nm	0.8–1.6 nm	300 nm
	$\sigma_{\text{MBE,MOVPE}} \sim 60 \times \sigma_{\text{LPE}}$		$\sigma_{\text{VPE,MOVPE}} \sim 200 \times \sigma_{\text{LPE}}$	

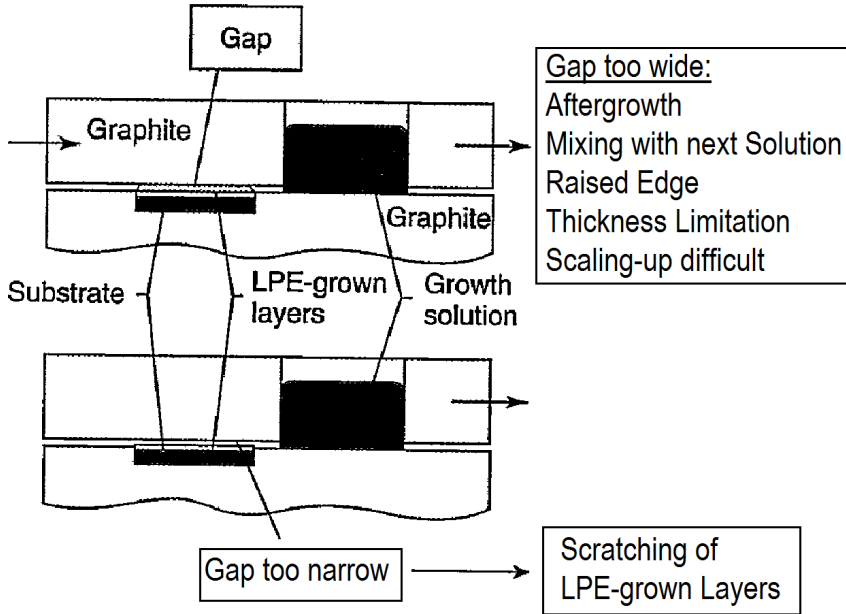
**T. Nishinaga and H.J. Scheel in Advances in Superconductivity VIII Vol.1, editors H. Hayakawa and Y. Enomoto, Springer Tokyo 1996, 33.**



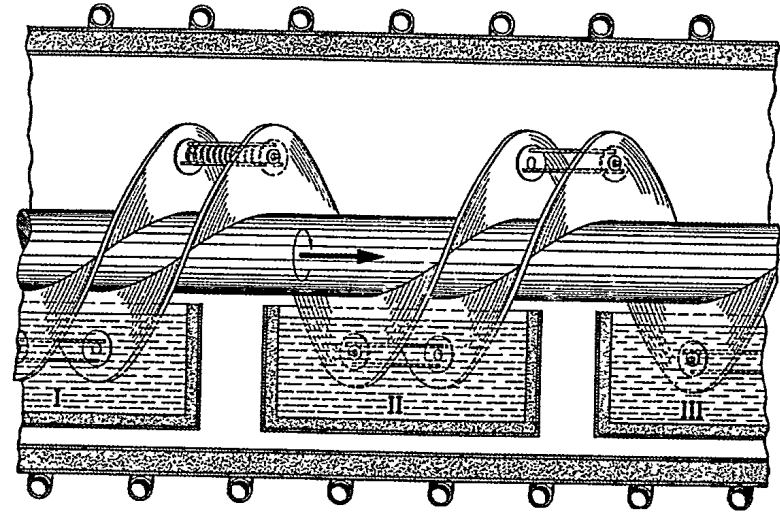
**Eight epitaxial growth modes**  
***in Crystal Growth Technology,***  
**editors H.J. Scheel & T. Fukuda**  
**Wiley 2003, Chapter 28**

# Liquid Phase Epitaxy

## Problems in Slider Technology



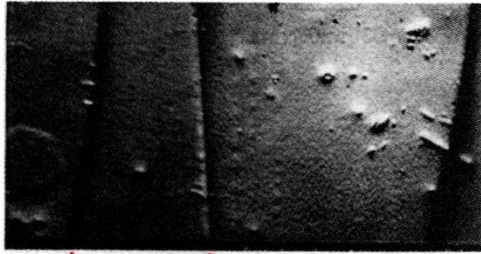
## Sliding-free Technology for Mass Production



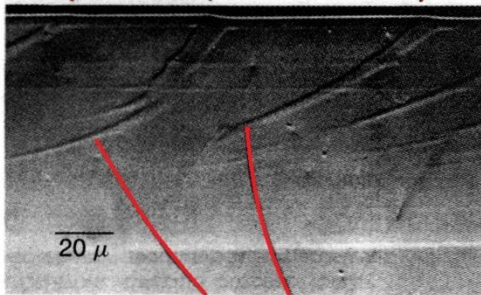
US Patent 3,858,553 (Jan.7, 1975, H.J.Scheel /IBM, J. Crystal Growth 42(1977)301 - 308 (ICCG-5 Boston).

## Macrostep-Induced Striations

LPE of GaP  
As-grown surface



Cleaved and etched  
in HF + H<sub>2</sub>O<sub>2</sub>  
+ 3H<sub>2</sub>O at 20°C

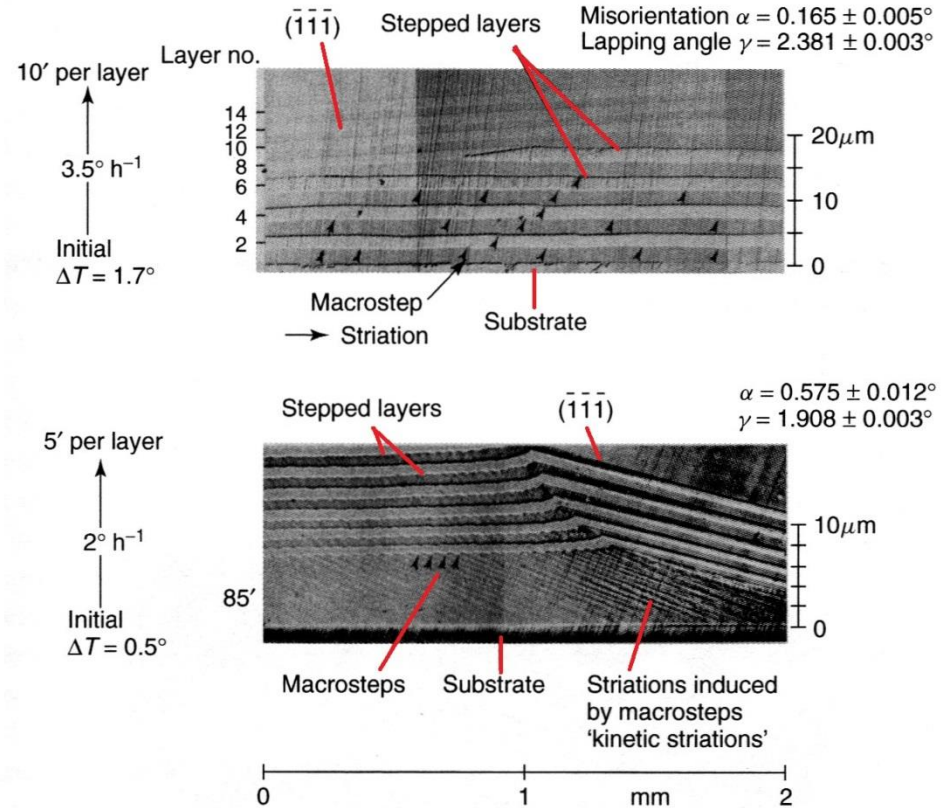


Increasing step bunching

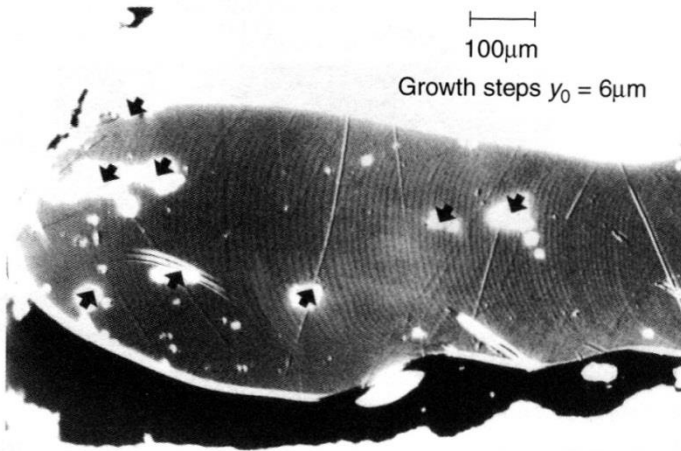
Growth  
Direction

J. Nishizawa and Y. Okuno, Cetniewo, Poland 1978

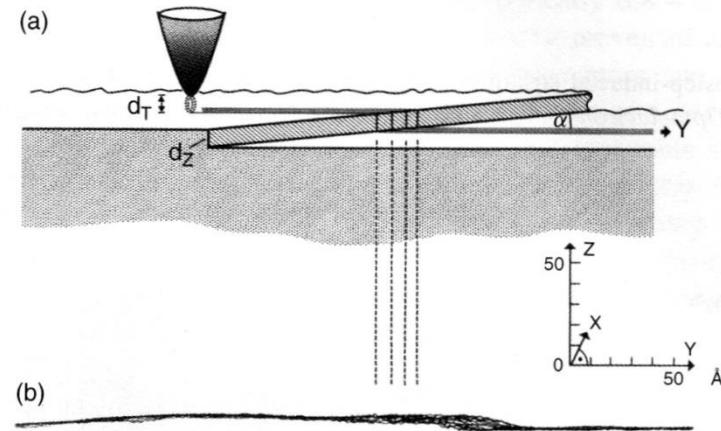
## Transition to Faceting in Multilayer LPE



Appl. Phys. Letters 37 (1980) 70-73, H.J. Scheel



Differential interference contrast microscopy (Nomarski) of GaAs (111) facet. Step distances of  $6 \mu\text{m}$  are visible.



Step heights of  $6.5 \text{ \AA}$  are measured by STM. (a) Principle, (b) Multi scan by STM.

H.J. Scheel, G. Binnig and H. Rohrer: Atomically Flat LPE-grown Facets Seen by Scanning Tunneling Microscopy, J. Crystal Growth 60(1982)199 - 202.

# Comparison of PVD/CVD Surfaces with LPE Surfaces of High-Temperature Superconductors

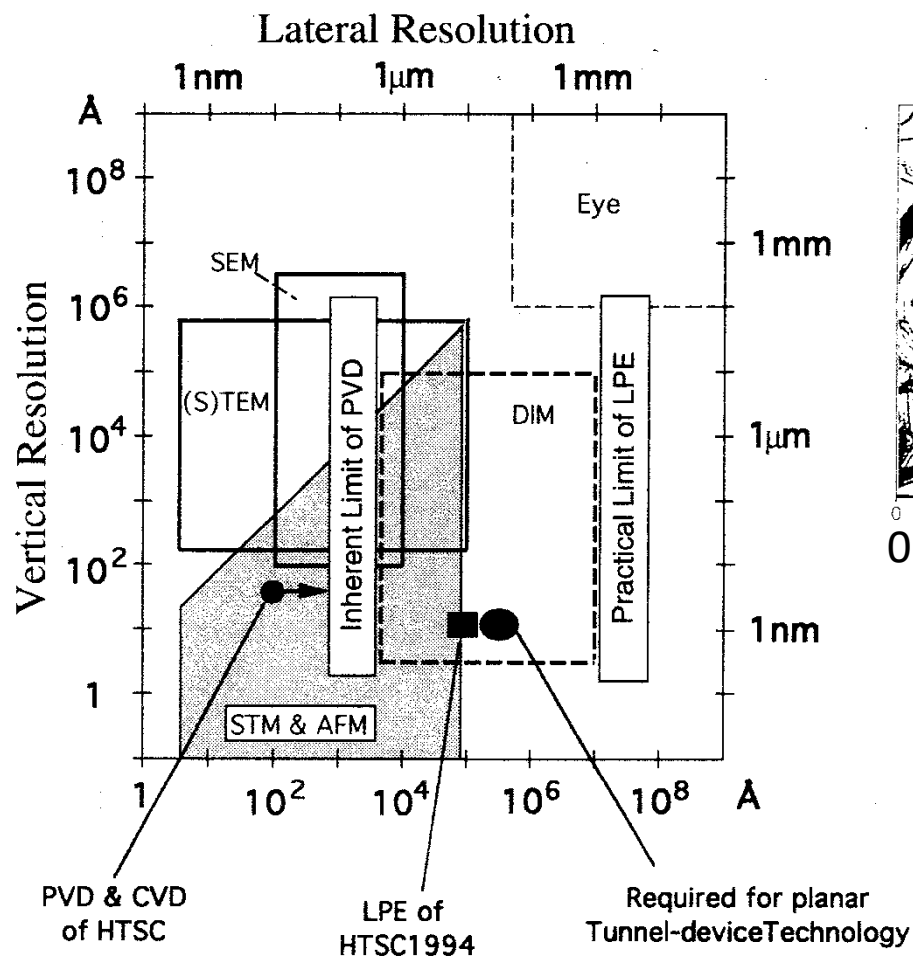


Figure 11. Surfaces (step heights and lateral step distances) of YBCO grown by PVD, CVD, and LPE and the detection limits of electron microscopes (SEM, TEM), scanning tunneling microscopy (STM) and atomic force microscopy (AFM), and of the optical differential interference contrast (Nomarski) microscope (DIM). Also shown are the inherent limit of PVD and the practical limit of LPE by vertical bars, and the step distances required for a planar HTSC tunnel-device technology.<sup>34</sup>

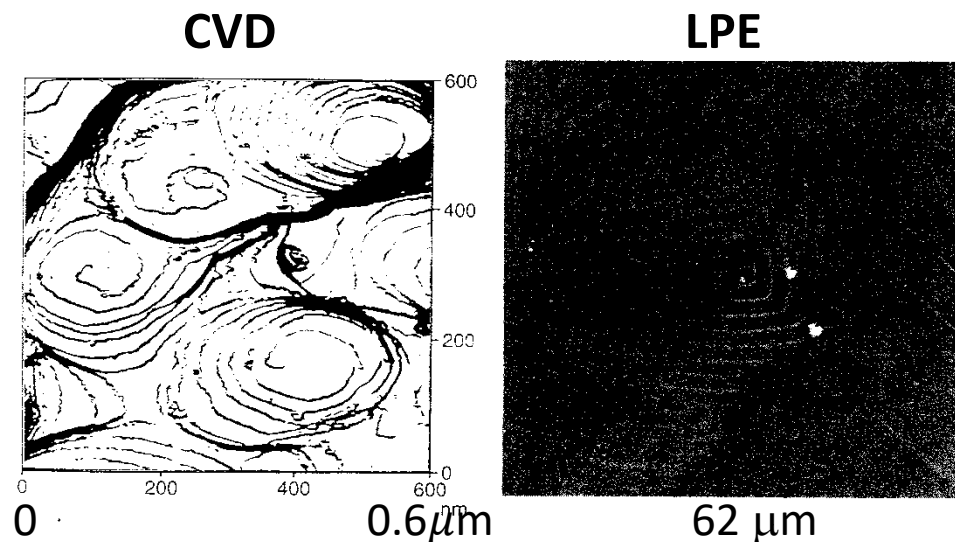


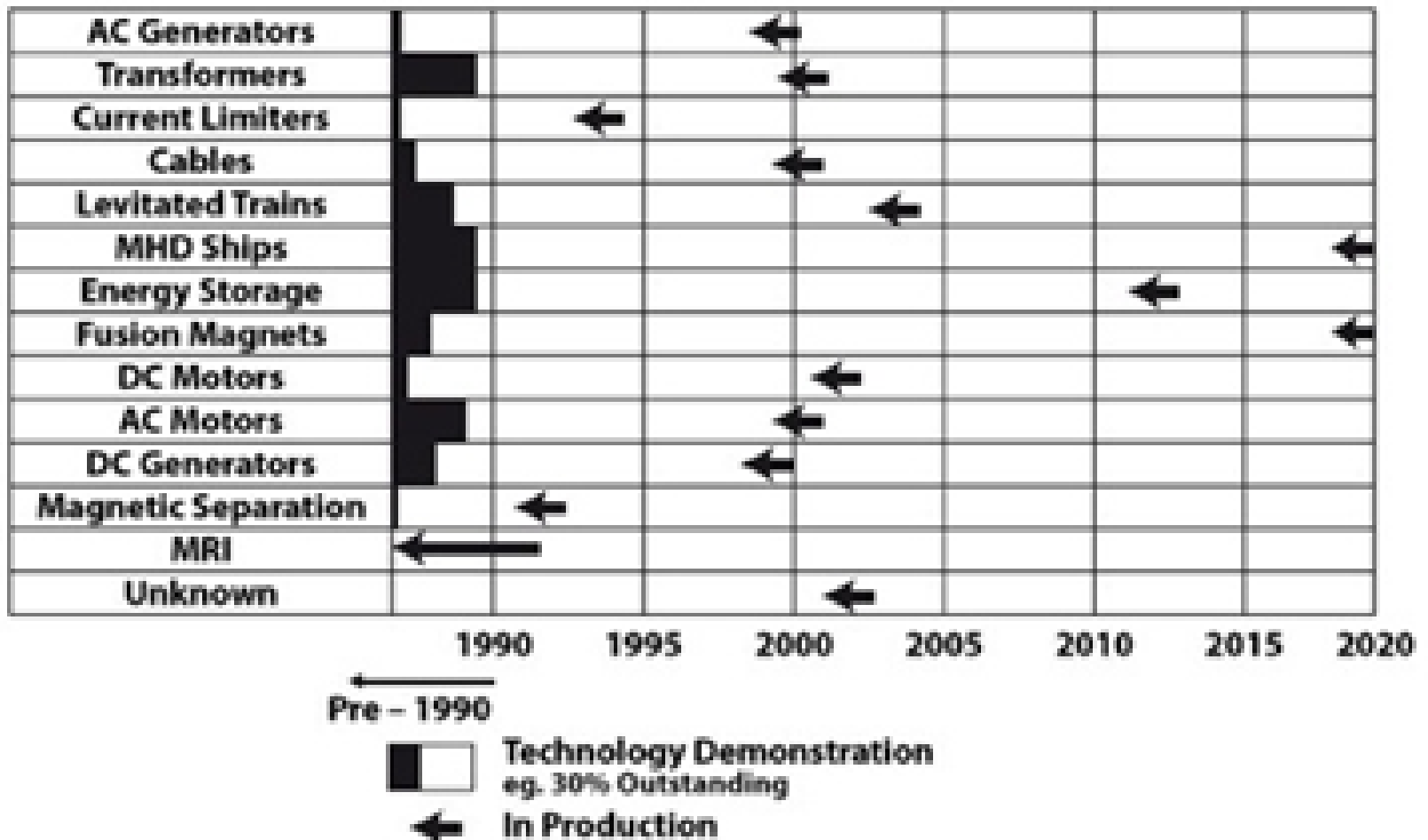
Figure 12. Typical spiral structures of (a) CVD-grown<sup>36</sup> and (b) LPE-grown YBCO layers. The LPE spiral has a diameter of 62  $\mu\text{m}$ . Note the different scales which correspond to  $>3 \times 10^8$  spiral islands/cm<sup>2</sup> in vapor-grown and to about  $10^3$  spirals/cm<sup>2</sup> in LPE-grown layers.

- Monosteps on extremely flat  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  surfaces grown by liquid-phase epitaxy, *Appl. Phys. Lett.* **65** (1994)901-903. (H.J. Scheel, C. Klemenz, F.-K. Reinhart, H.P. Lang, and H.-J. Güntherodt)
- *Materials Engineering Problems in Crystal Growth and Epitaxy of Cuprate Superconductors*, *MRS Bulletin* **19**(1994)26-32 (H.J. Scheel)

# Predicted Applications of High-Temperature Superconductors for Energy Storage & Electricity Transport and for Fusion Magnets

1991/1994

## Prospects for 21st century



# High-Temperature Superconductivity HTSC

Discovery 1986 initiated in the IBM Zurich Research Laboratory, Switzerland  
K.A.Müller & J.G.Bednorz 40K; C.W.Chu & M.K.Wu et al. at Houston/Texas 92K !!!  
Details in [www.hans-scheel.ch](http://www.hans-scheel.ch)

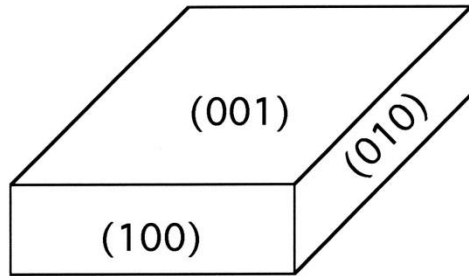
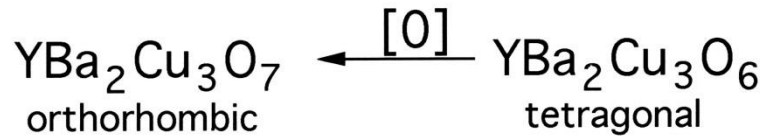
- \* **HTSC for Energy Saving:** Motors, Generators, Current Limiters, MHD Ship Drive, Levitating Trains, etc.
- \* **HTSC Cables for Electricity Transport:** No Loss
- \* **HTSC for Energy Storage:** Flywheels
- \* **HTSC for Computers:** Josephson Devices
- \* **HTSC for Medicine:** Squid Detectors

**Problem: Not physics, but Materials & Crystal Growth Problems, Physical Chemistry, Mechanical Engineering for Fabrication of Reliable Layers, Cables, Coils.**

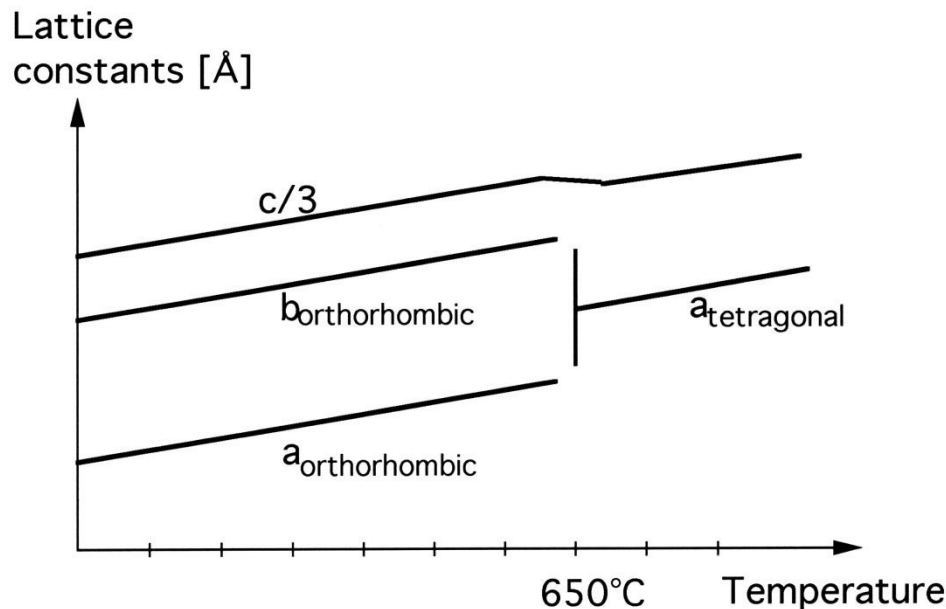
**Chance with educated Crystal Technologists in Future**



## Oxidation and Epitaxy Problems with High-Tc Superconductors



$$\begin{aligned}
 D [0] // [010] \\
 \gg D [0] // [100] \\
 \gg D [0] // [001]
 \end{aligned}$$



Growth of  $\text{YBa}_2\text{Cu}_3\text{O}_6$  which has to be oxidized to  $\text{YBa}_2\text{Cu}_3\text{O}_{6.85}$  to become superconducting at 92K.

### Problems:

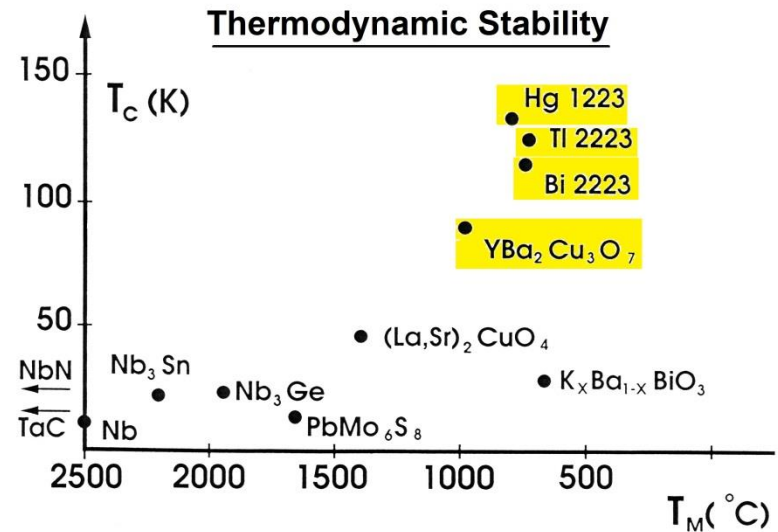
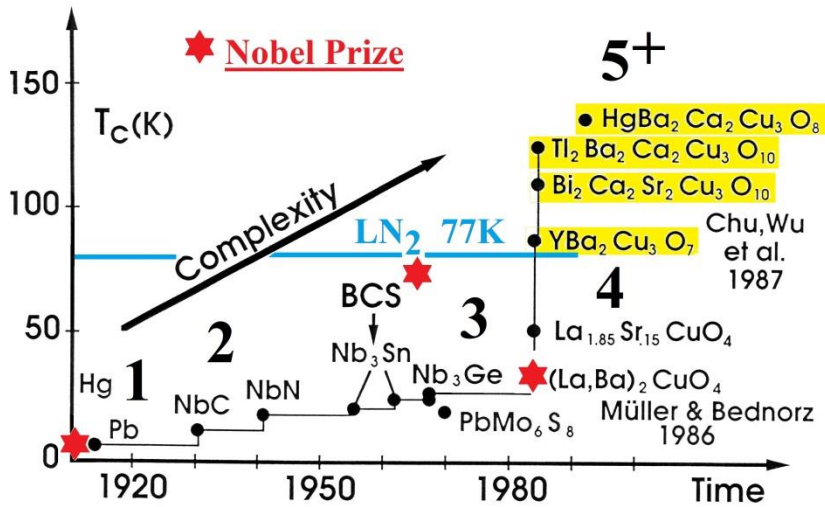
Phase transition,  
 Anisotropic diffusion coefficients,  
 Thermal expansion difference  
 Mechanical properties.

Goal: Prevent cracking, twinning,  
 grain boundaries/dislocations,  
 strain/bending.

### Similar problems in epitaxy:

Substrate with low misfit, fitting  
 thermal expansion and phase  
 transition, mechanical properties..

A task for well-educated crystal technologists in collaboration with physico-chemists, mechanical engineers, structure engineers.

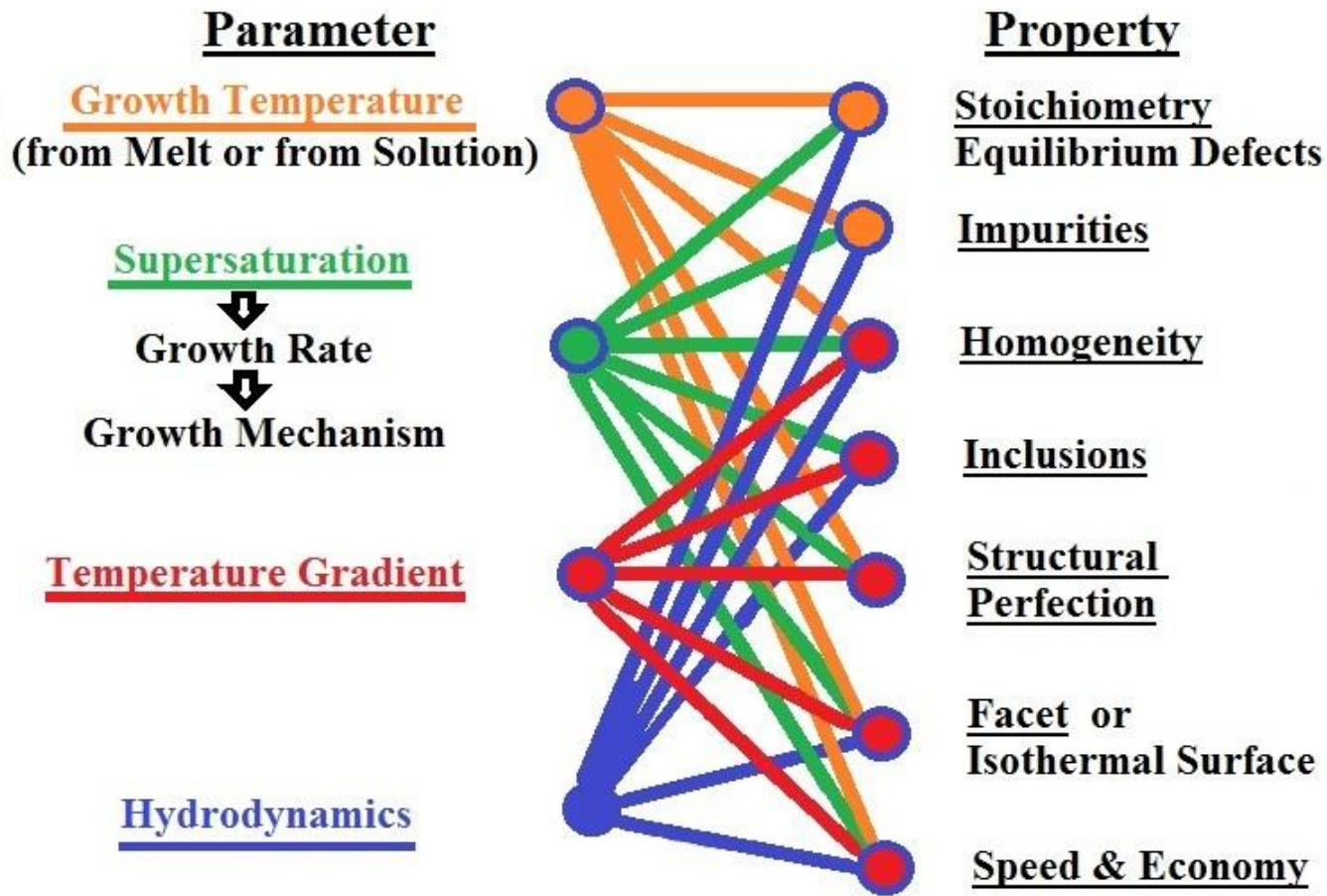


1. **Problem:** Define the optimum HTSC compound which has sufficient thermodynamic stability to develop Crystals, Epitaxial Layers, Coils etc. for Applications in Energy / Electricity Technology, as Squid Detectors in Medicine, as Josephson Devices in Ultrafast Computers, and for applications in Fusion Energy.

2. **Problem:** Develop a substrate for the optimum HTSC compound which prevents cracking, twinning and formation of dislocations/grain boundaries upon cooling from synthesis temperature, from oxidation and from phase transition.

- *Materials Engineering Problems in Crystal Growth and Epitaxy of Cuprate Superconductors*, Material Research Bulletin **19**(1994)26-32 (H.J. Scheel).

# Effect of Growth Parameter on Crystal Property



Multi-Parameter Processes  
 Approach: Trial & Error  
 Systematic  
 Intuitive / Empirical  
 Design of Experiment  
 Fully Scientific

Complexity  
 Multidisciplinary  
 Scaling / Dimension Problem

Art  
 ↓  
 Science of Crystal Growth

Other Parameters  
 Chemicals Purity  
 Solvent  
 Transport Agent  
 Dopant  
 Crucible: Composition,  
 Size, Shape, Purity  
 Atmosphere; Gravity

# "Sufficient" Characterization

High - Tc Update Vol. 5 No. 19, Oct.1, 1991 p.3

## Overviews

*Problems in* the epitaxial growth of high- $T_c$  superconductors are reviewed by H. J. Scheel et al. (Swiss Federal Institute of Technology, Lausanne), who discuss epitaxial deposition techniques and parameters, growth mechanisms and film orientation, substrates, and characterization. The authors stress that, since it is very difficult to achieve reproducibility of growth, "sufficient" characterization of the epitaxial films and surfaces is of utmost importance. The term "sufficient" means all those chemical and structural aspects of the layer which have or may have an influence on the measured physical phenomenon or on the specific application. The authors also note that film-growth processing with lower growth (substrate) temperatures (below 500°C, if possible) is desired for combining semiconductor and superconductor technologies (45 references).

**NATO Advanced Study Institute**  
July 10-23, 1994 Greece  
Prof. John Clem, AMES Laboratory  
Editor of High-Tc Update:  
No HTSC paper with  
sufficient characterization!  
No reproducibility  
in solid-state physics of  
high-Tc superconductors!

Responsibility of Physicists  
and of Crystal Growers!

# Single Optimum Technology for Growing a Specific Crystal or Epilayer with Specifications for a Given Application

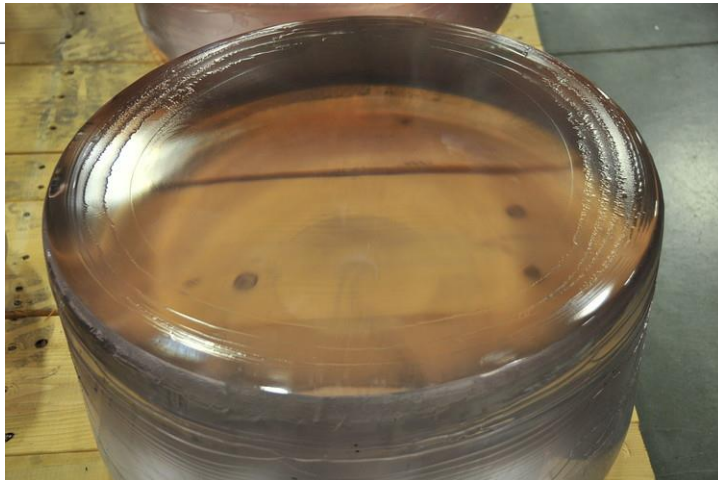
based on

- ▶ Thermodynamics / Phase Diagrams
- ▶ Principles of Crystal Growth and Epitaxy
- ▶ Energy Consumption, Infrastructure
- ▶ Economics, Resources
- ▶ Timeliness
- ▶ Ecology

**Requirements:** ▶ **Education of Crystal Technologists**  
Engineers and Scientists with multi-disciplinary Education plus special Education in Crystal Fabrication Technology, Crystal Machining, Epilayer Growth, Surface Technologies, and Crystal, Epilayer and Surface Characterization

▶ **Workshops and Schools on Crystal Technology**

➡ 7th International Workshop on Crystal Growth Technology  
IWCGT - 7 Potsdam / Berlin July 2 - 6, 2017



- Results:**
- ▶ Saving of more than 90% of Development Costs for Crystals and Epilayers, of Resources, and of Energy
  - ▶ Enhanced Developments of Solid State Sciences and of Technologies
  - ▶ Improved Reputation of the Field Crystal Growth

## Examples:

1. **Reliable Josephson Device / Squid Technology based on High-T<sub>c</sub> Superconductors** demands atomically flat surfaces due to short coherence lengths and required nm-thin barrier layers. 1989 More than 1000 groups worldwide tried to achieve this by about 10 different methods of vapor epitaxy: Island formation, maximum interstep distance 50 nm. *Only by liquid phase epitaxy near equilibrium can atomically flat surfaces be achieved with interstep distances of more than 10 μm.*
2. **GaN:** *Only by liquid phase epitaxy on GaN substrates can low dislocation densities required for highest-efficiency and longest-lifetime light-emitting diodes and power devices be achieved (not by MBE or MOCVD, exception immiscibility).*
3. **Growth of Homogenous Crystals of Solid Solutions at Highest Yield and Without Striations** not by reduced convection or in microgravity. *Only by optimized forced convection can economic growth of solid solutions and of doped crystals be achieved.*
4. **Apple's dream of sapphire screen on iPhone and iPad:** Apple spent 439 Million \$ and GT 900 Million \$ to build a factory in Mesa/Arizona and 2036 large HEM furnaces and hired 700 employees for producing 262 (164)kg sapphire boules\*. Agreement signed by Apple and GT October 31, 2013, GT bankruptcy October 6, 2014. *Wall Street Journal November 20, 2014. \*30x of largest competitor.*

Poly on top



Crack initiated from seed



Thermal crack in cool down



Crack from blackbody



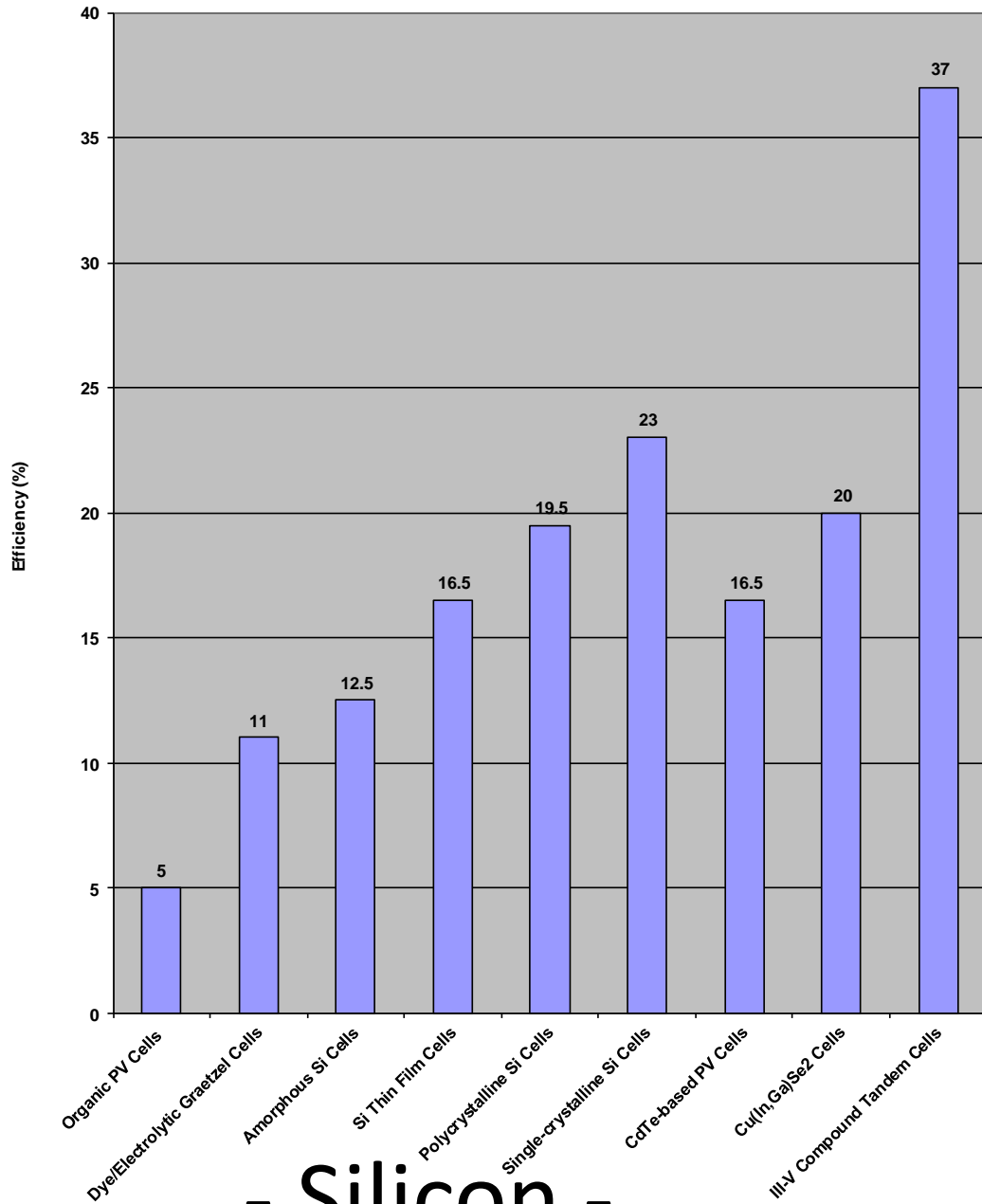
Spiral crack



Horizontal crack



Best Efficiencies of Research Solar Cells  
Data from T. Surek/NREL 2004



- Silicon -

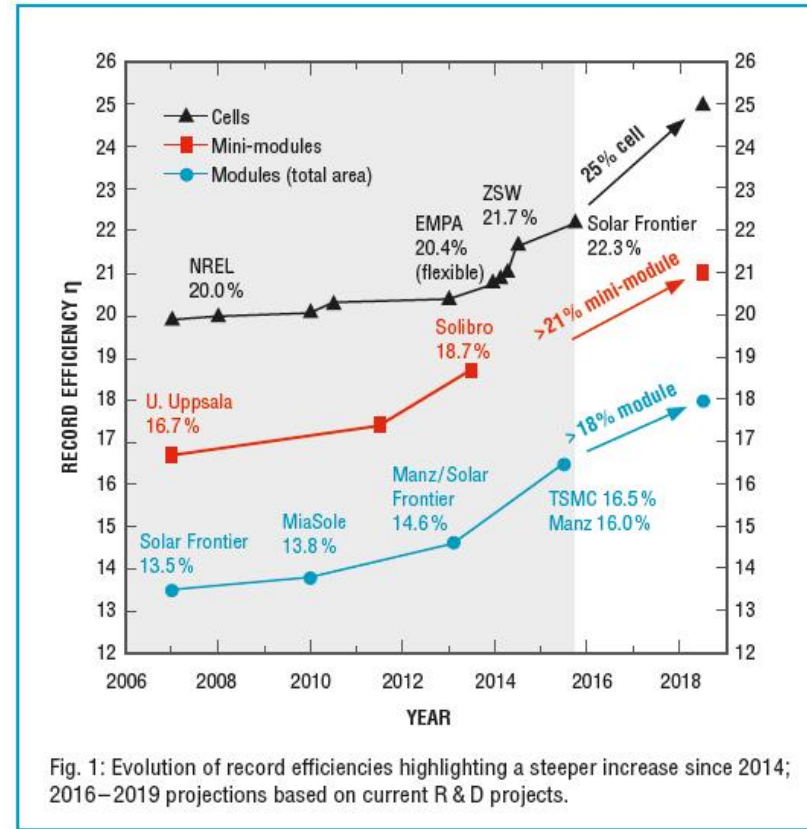
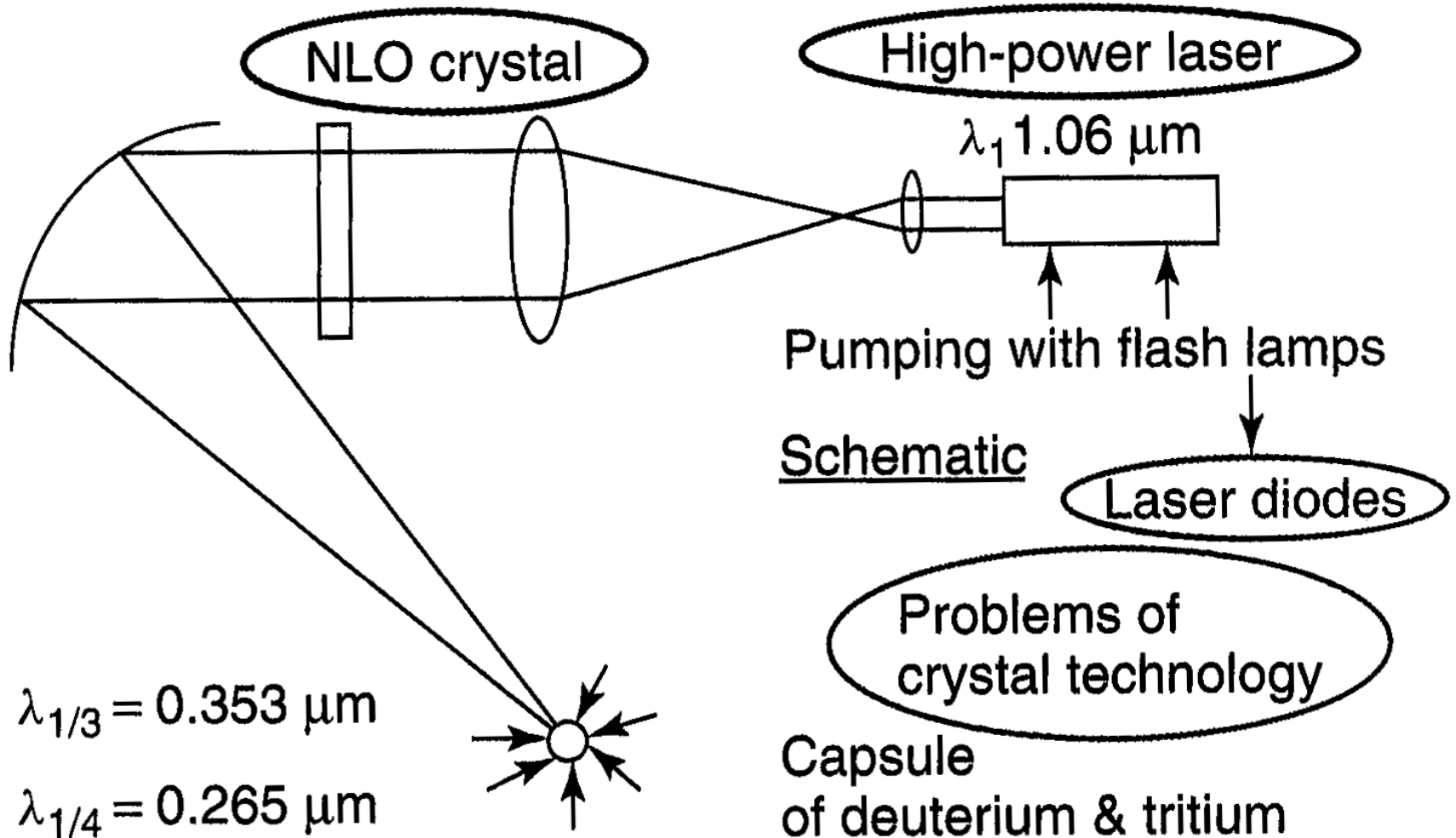


Fig. 1: Evolution of record efficiencies highlighting a steeper increase since 2014; 2016–2019 projections based on current R & D projects.

CPV with  
Optimum Growth Process?

*Has Fusion Energy by Magnetic Inclusion (Tokamak) a Chance as long as the Problem of the "First Wall" is not solved?*

## Laser Crystals and NLO Crystals for Laser Fusion Energy



# CONCLUSIONS / REQUIREMENTS

## Required Progress in

- Theoretical Understanding of Growth Parameters and Growth Processes, Develop Optimum Technology
- Education of Crystal Technologists with Emphasis on Epitaxy Problems and on **Energy Problems**
- Solve the Relevant Crystal-, Epitaxy- and Fabrication Problems of High-Temperature Superconductivity with one Optimum HTSC Compound with  $T_c$  above Boiling Point of Liquid Nitrogen
- **Looking back 50 years work: It was always challenging and fun to work in Crystal Growth Technology**

**Thank You**

**for giving me the DGKK-Award and for listening**







**Tsunami  
Sumatra  
26.12.2004**



**Tsunami Tohoku,  
Japan  
11.3.2011**



**Hurricane  
Katrina  
29.8.2004**



**Typhoon Haiyan,  
Philippines  
8.11.2013**

After Hurricane Katrina  
USA/Louisiana  
29.8.2005

After Haiyan  
typhoon Philippines  
8.11.2013

<b>Sumatra Tsunami 2004</b>	<b>210' 000 Fatalities</b>	<b>Damage 10 billion \$</b>
<b>Katrina Hurricane 2005</b>	<b>1'300 Fatalities</b>	<b>Damage 125 billion \$</b>
<b>Tohoku Tsunami 2011</b>	<b>19'000 Fatalities</b>	<b>Damage 300 billion \$</b>
<b>Haiyan Typhoon 2013</b>	<b>8'000 Fatalities</b>	<b>Damage 2.86 billion \$</b>
<b>Total</b>	<b>238'300 Fatalities</b>	<b>Damage 438 billion \$</b>

+ global & Fukushima consequences

## **Vertical Submerged Barriers to Prevent Flooding and Erosion**

**Hans J. Scheel**

**Scheel Consulting, Switzerland, [hans.scheel@bluewin.ch](mailto:hans.scheel@bluewin.ch)**

**With Contribution from Hisham Elsafti & Hocine Oumeraci**  
Leichtweiss-Institute for Hydraulic Engineering, Techn. University Braunschweig, Germany  
[h.el-safti@tu-braunschweig.de](mailto:h.el-safti@tu-braunschweig.de); [h.oumeraci@tu-braunschweig.de](mailto:h.oumeraci@tu-braunschweig.de)

### **Results of Numerical Modelling (H.El-Safti)**

---

**Assumption:**

**Strong Tsunami: At 4000m water depth**

Speed 713 km per hour (198m/s), wave height 1.00m

**At the impermeable TFB barrier at 30m water depth**

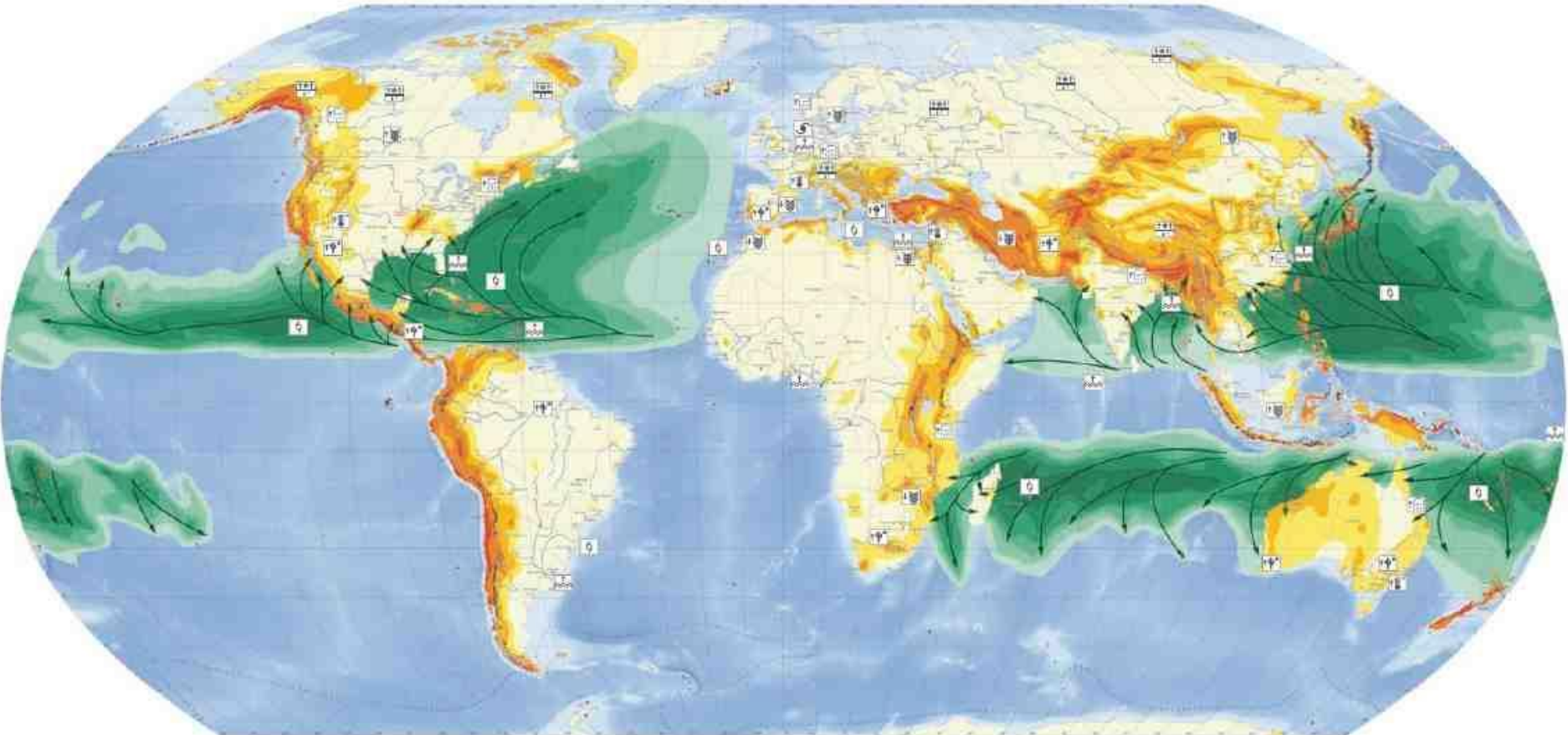
Speed 65 km per hour (18.1m/s), wavelength 188.92m,  
wave height without barrier 3.40m

Runup x 2.0566 = **6.992m wave height** at the barrier

Pressure 66.587kN/m<sup>2</sup> = **6.66t/m<sup>2</sup>**

Horizontal force per meter at seabed level = **223.04t/m**

# NATHAN WORLD MAP OF NATURAL HAZARDS



### EARTHQUAKES

- Zone 0: MM V and below
- Zone 1: MM VI
- Zone 2: MM VII
- Zone 3: MM VIII
- Zone 4: MM IX and above

Probable maximum intensity (MM-Modified Mercalli scale) with an exceedance probability of 10% in 50 years (equivalent to a "return period" of 475 years) for medium subsoil conditions.

Large city with "Mexico City effect"

### TROPICAL CYCLONES

Peak wind speeds (in km/h)\*

- Zone 0: 76-141
- Zone 1: 142-184
- Zone 2: 185-212
- Zone 3: 213-251
- Zone 4: 252-299
- Zone 5: ≥ 300

\* Probable maximum intensity with an exceedance probability of 10% in 50 years (equivalent to a "return period" of 100 years).

Typical track directions

### VOLCANOES

- Last eruption before 1800 AD
- Last eruption after 1800 AD
- Particularly hazardous volcanoes

### TSUNAMIS AND STORM SURGES

- Tsunami hazard (pacific sea wave)
- Storm surge hazard
- Tsunami and storm surge hazard

### ICEBERG DRIFTS

Extent of observed iceberg drifts

### CLIMATE IMPACTS

Main impacts of climate change already observed and/or expected to increase in the future.

- Change in tropical cyclone activity
- Intensification of extratropical storms
- Increase in heavy rain
- Increase in fires/droughts
- Increase in droughts
- Threat of sea level rise
- Permafrost thaw
- Improved agricultural conditions
- Unfavourable agricultural conditions

### POLITICAL BORDERS

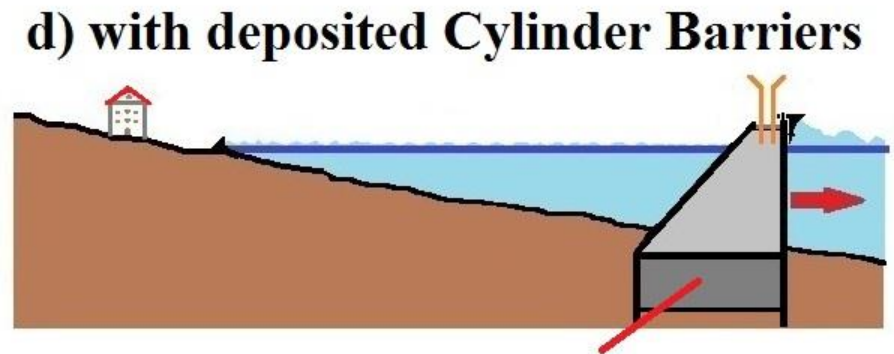
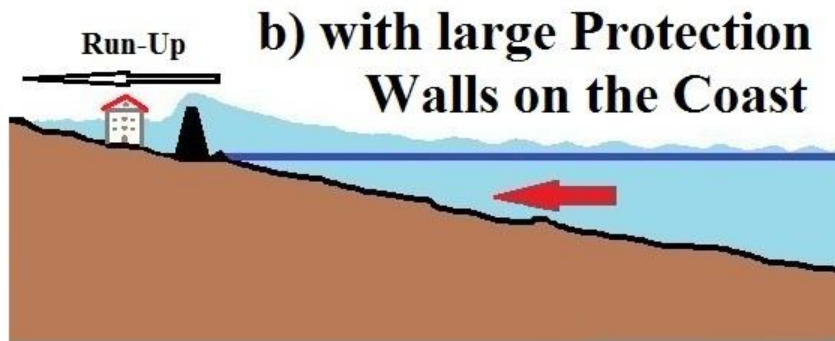
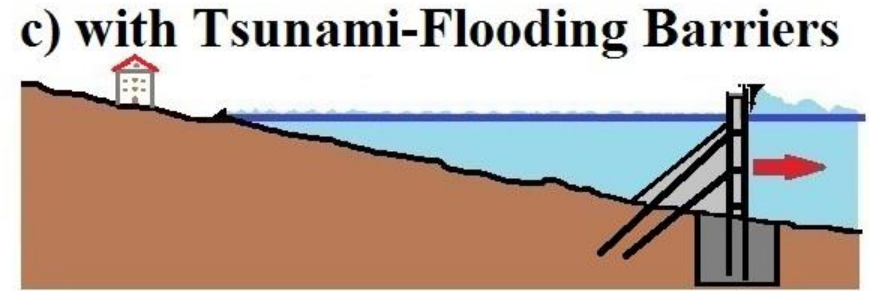
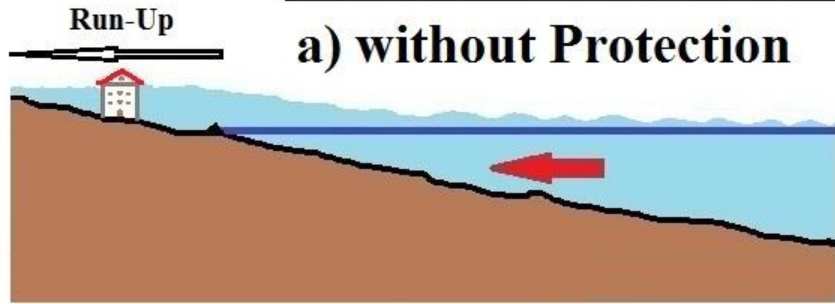
- State border
- State border controversial (political borders not binding)

### CITIES

- Denver > 1 million inhabitants
- San Juan 100,000 to 1 million inhabitants
- Maui < 100,000 inhabitants
- Berlin Capital city

*Data sources:*  
 Bathymetry: Amanti, C. and B. W. Eckins, ETOPO1 1 Arc-Minute Global Relief Model-Procedure, Data Source and Analysis, National Geospatial Data Center, NESDIS, NOAA, U.S. Department of Commerce, Boulder, CO, August 2008. Extratropical storms: KNMI (Royal Netherlands Meteorological Institute), Temperature/Precipitation 1978-2007: Climate Research, UEA, University of East Anglia, Norwich.

# Four Coastal Situations with Tsunami Impact

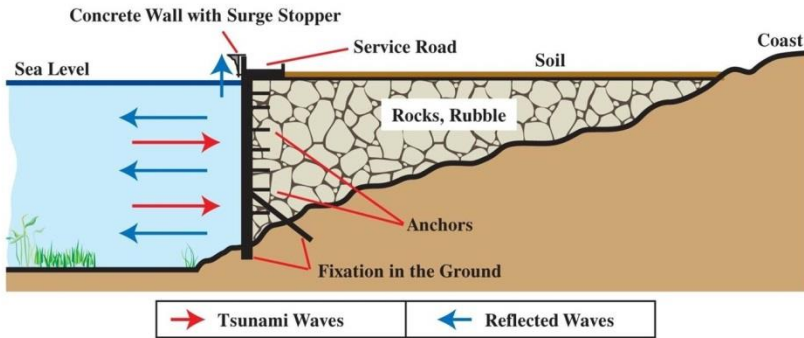


Concrete Foundation

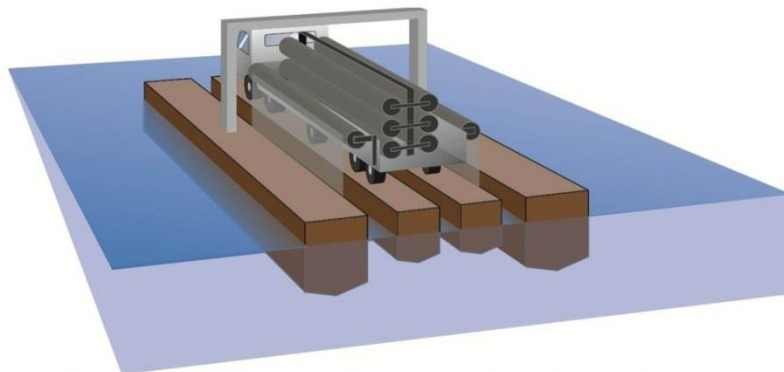
**Tsunami Impulse Waves**

**....Reach the Coast**

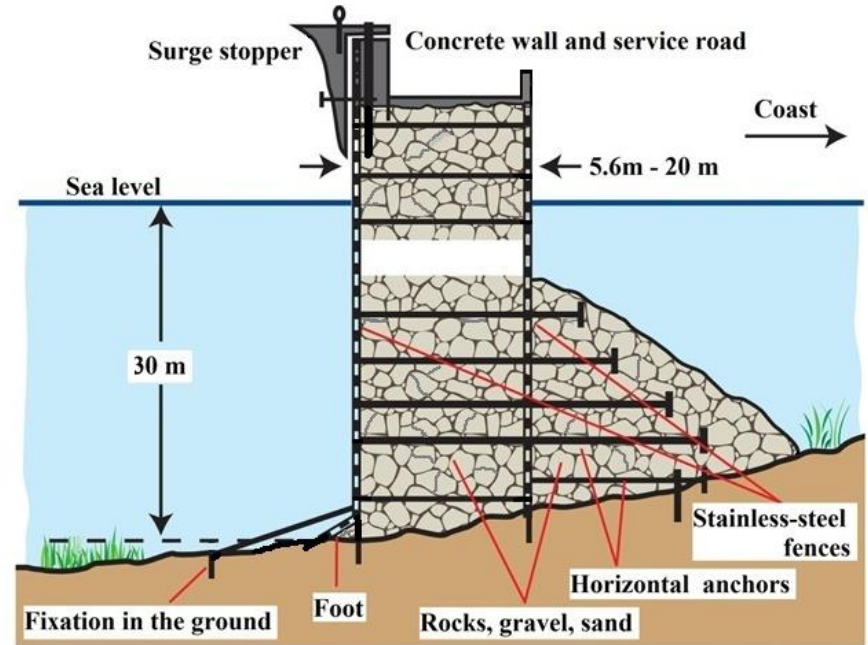
**....are Reflected before Reaching the Coast**



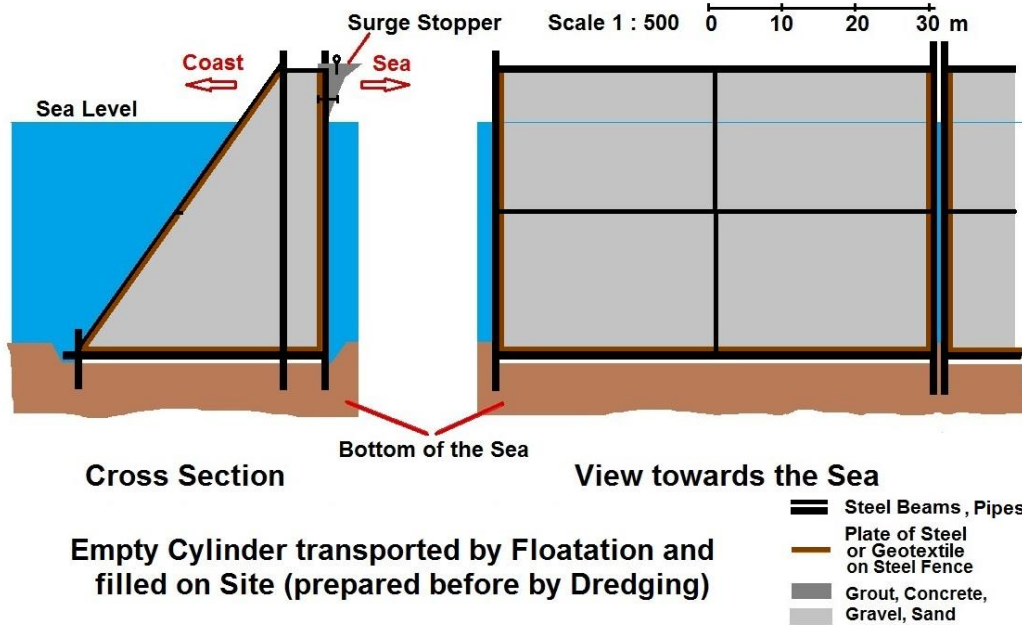
Schematic cross section of a vertical barrier in the sea which reflects the tsunami impulse waves. The gap between barrier and coast is filled up for land reclamation.



Schematic view of a truck on a double-pontoon simultaneously inserting two steel fences from fence rolls into the sea



Double-fence tsunami-flooding barrier with concrete road, walls and surge stopper, schematic cross section



**Dredging/cleaning of the sea floor  
and supply of sand/gravel to fill the cylinder barrier**  
(Van Oord Ship)

# Heights of Tsunami Waves

## Speed of Tsunami Wave

$$c = \sqrt{(g \times h)}$$

$g$  = Gravitational Acceleration

$h$  = Depth of Sea

## Height (Amplitude $A$ ) of Tsunami Wave

$$A^2 \times c = \text{constant}$$

(Energy Conservation)

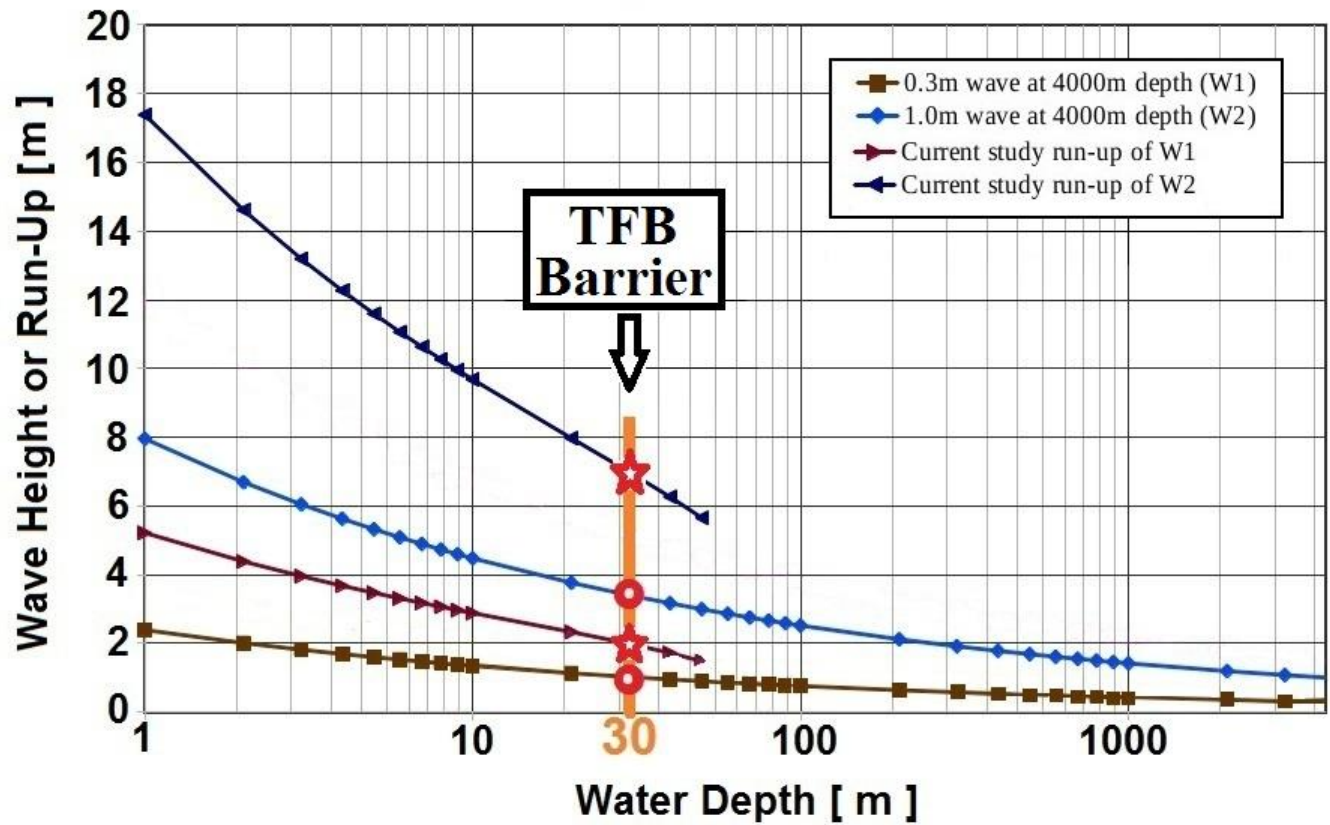
## Tsunami Wave Heights and Wave Velocities

(for original Tsunami Speed of 713km/hour at Ocean Depth of 4000m)

Depth	Speed (Km/h)	Wave Height
4000m	713	0.3m* 0.90m*
200m	160	0.63m 1.90m
40m	71	0.95m 2.85m
30m	62	1.02m 3.05m
20m	50	1.13m 3.39m

\*Assumed typical values

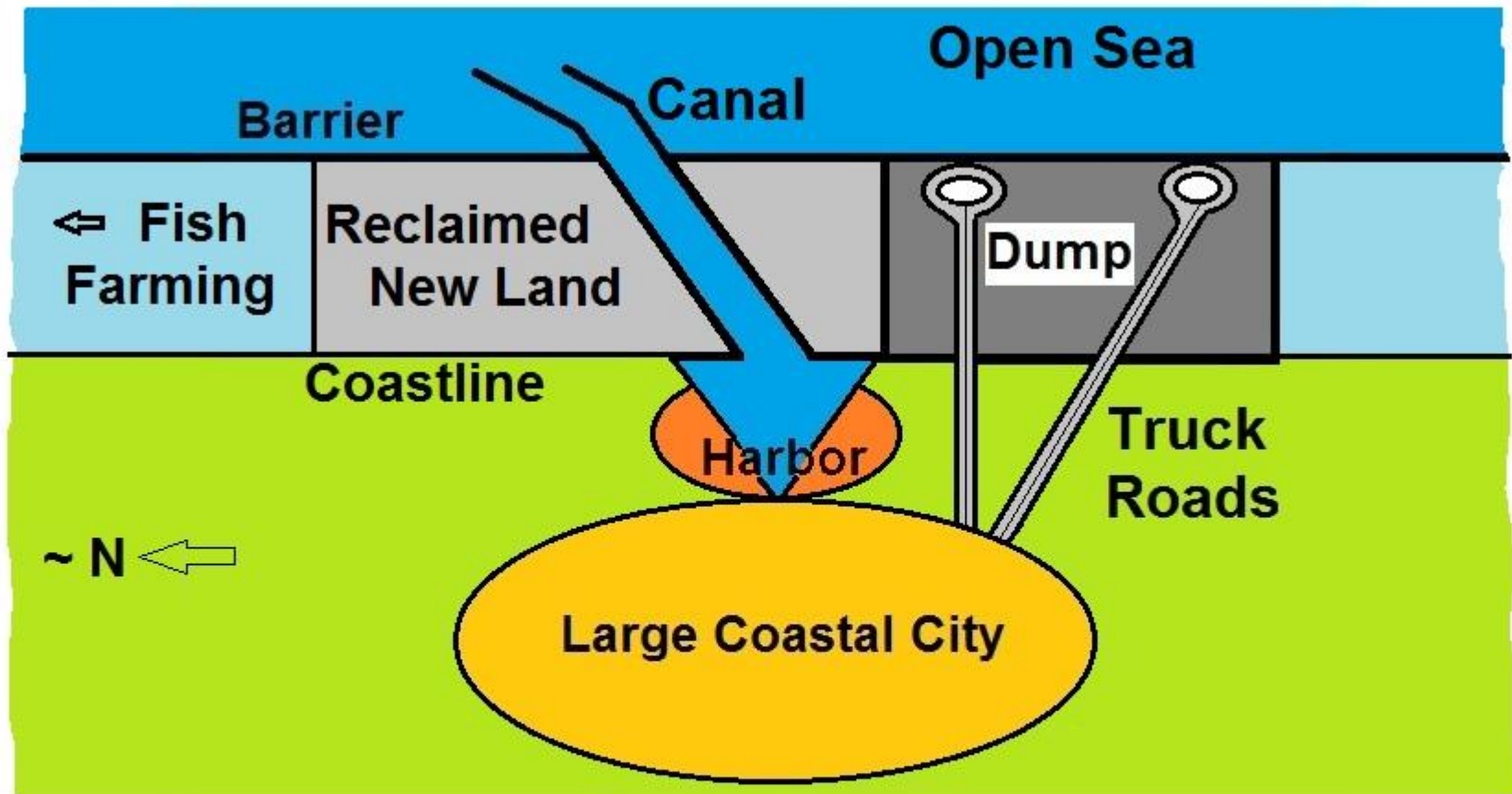




○ Wave Heights without Barrier

★ Run-Ups against vertical Barrier

**The height of an arriving Tsunami Wave is about doubled when stopped by a stable vertical Barrier**

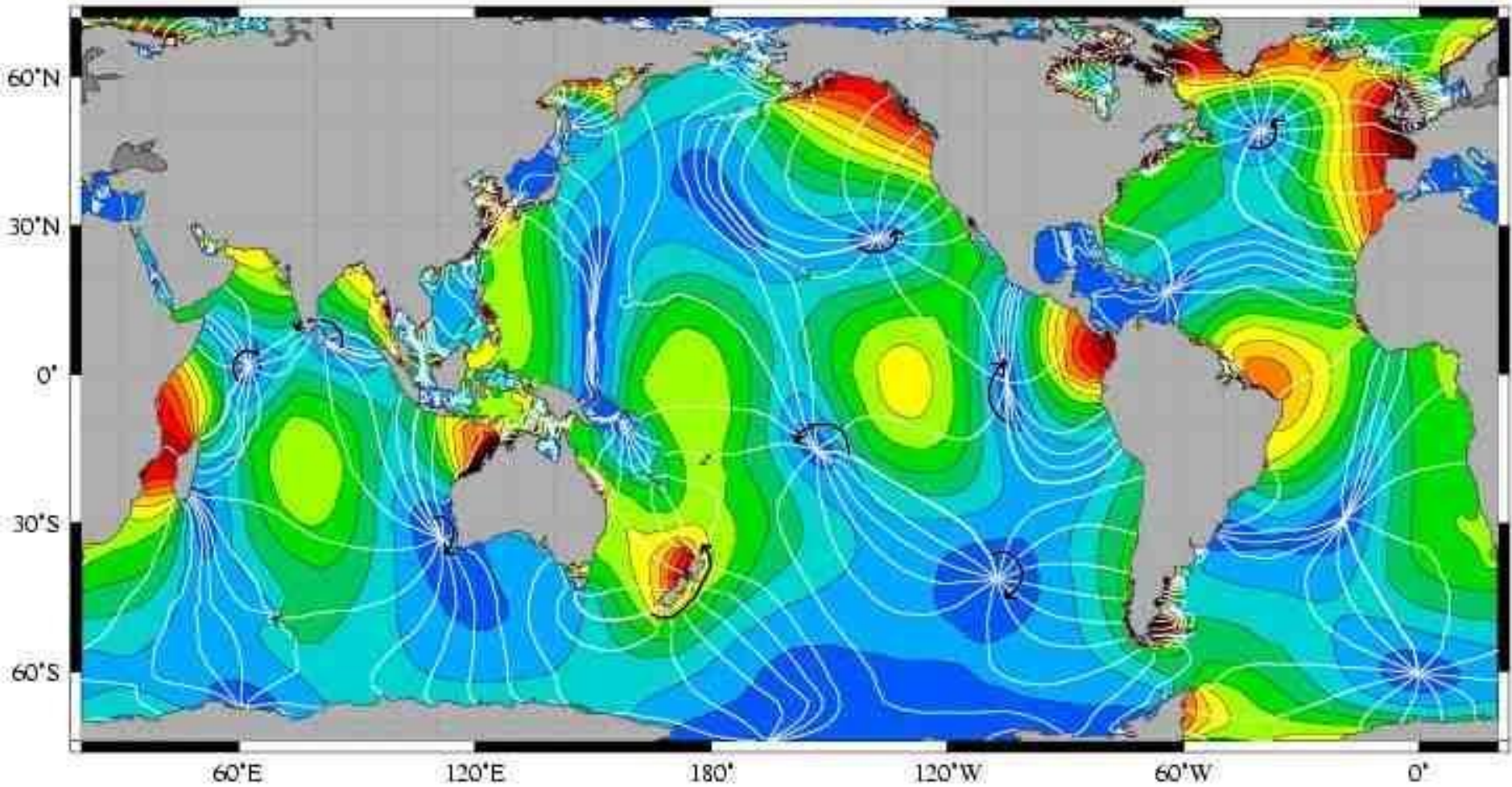


**Applications of Sea Reservoirs for Reclaiming New Land, for Fish Farming and, after Drainage, as Dump for Waste Disposal followed by Fill-up for more New Land, Top View**

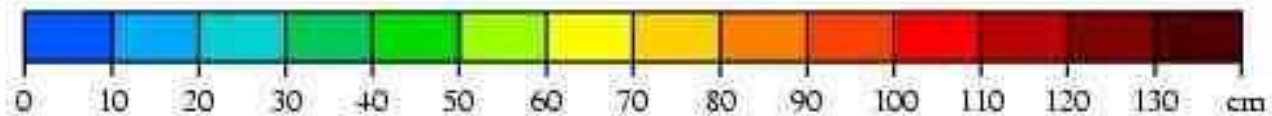
# Tidal Height Differences

GOT99.2

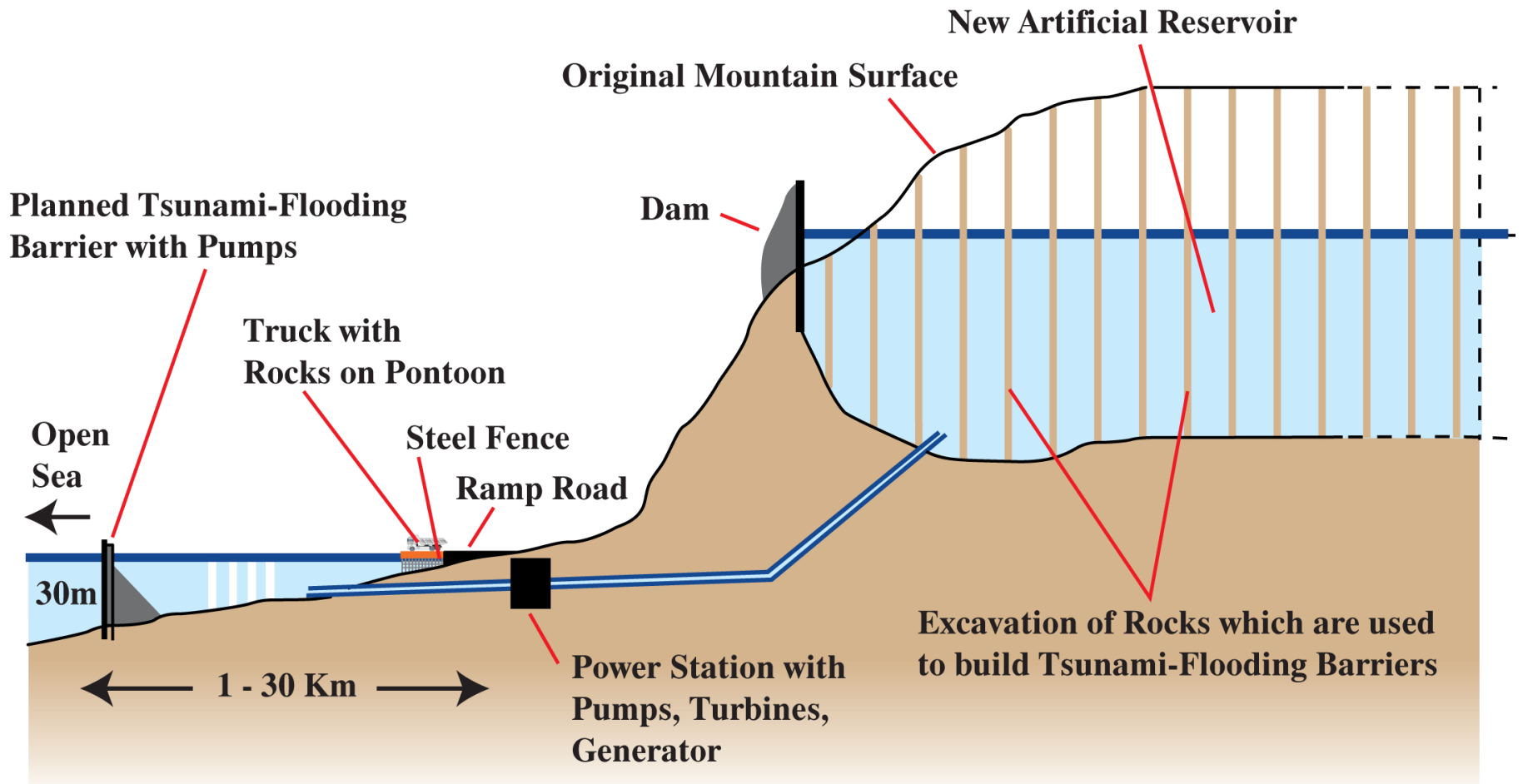
NASA/GSFC



R. Ray  
Space Geodesy Branch



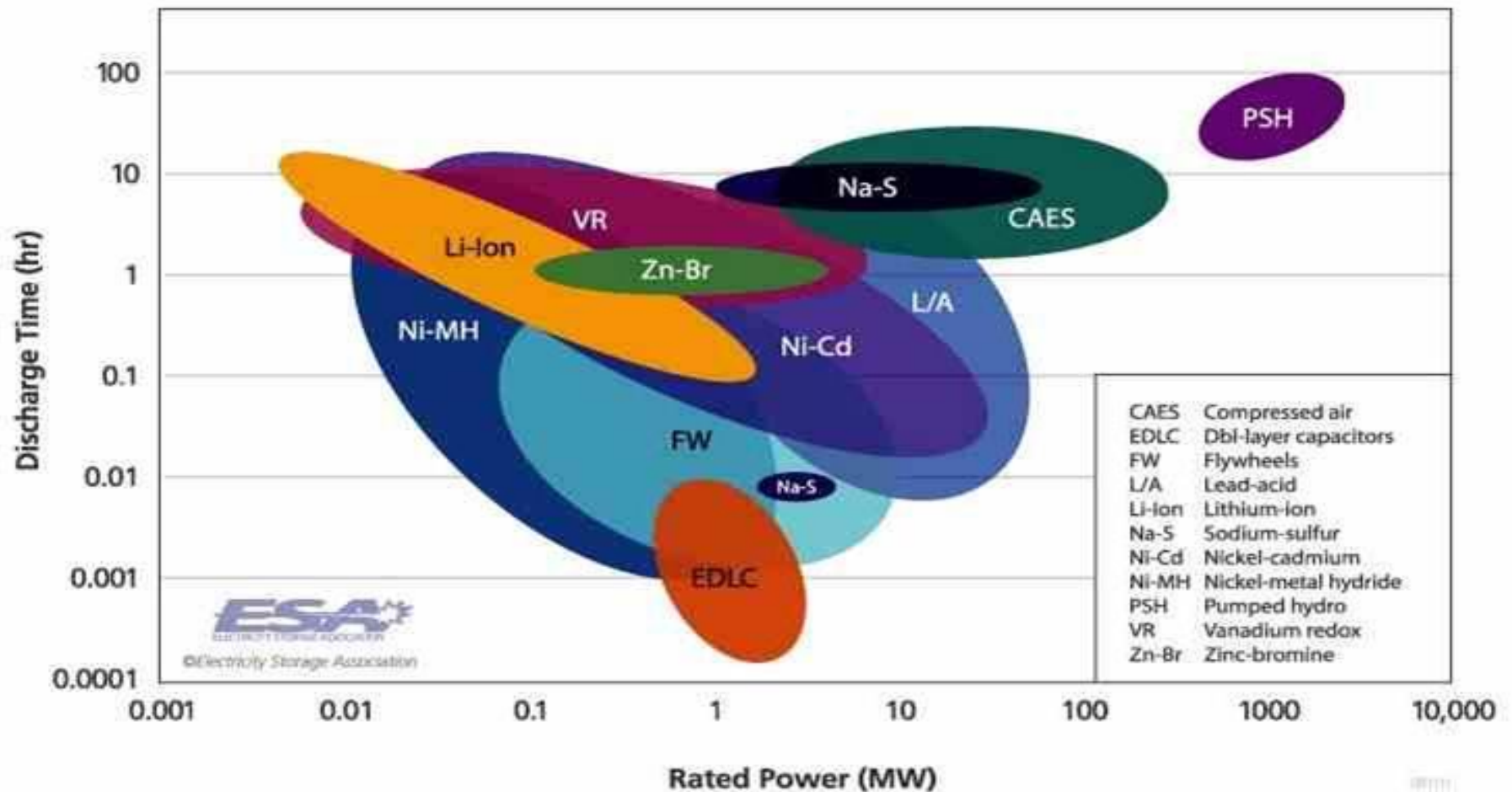
6/99



**Hydroelectric Energy Storage by Pumping Sea-Water to the Artificial Reservoir which is formed by Excavating Rocks for the Construction of Tsunami-Flooding Barriers (Schematic Cross Section)**

# System Ratings

Installed systems as of November 2008



# Humanity's Top Ten Problems for next 50 years

According to Richard Smalley  
Nobel Prize for Chemistry 1964  
Smalley 2003

- ENERGY
- WATER
- FOOD
- ENVIRONMENT
- POVERTY
- TERRORISM &  
WAR
- DISEASE
- EDUCATION
- POPULATION
- DEMOCRACY



2004	6.5	Billion People
2050	~ 10	Billion People

# 学位記

ハンス  
シール

西暦一九七七年五月十三日生

本学にて博士論文を提出し  
所定の審査に合格したため  
博士（工学）の学位を授与

す



三月十五日

東北大学

工第一五九二号

Tohoku University

Sendai Japan

This is to certify that

Hans J. Scheel

of Switzerland

born on May 13, 1937

has been duly awarded the Degree of

Doctor of Engineering

having passed the prescribed examination

on his thesis for the doctorate

in Tohoku University.

March 15, 1995

*Jun-ichi Nohjima*

President.

Tohoku University

# АКАДЕМИЯ ИНЖЕНЕРНЫХ НАУК

Российской Федерации

На основании Устава АКАДЕМИИ ИНЖЕНЕРНЫХ НАУК  
Российской Федерации

**ИЗБРАЛА**

*Ханса Шееля*

ИНОСТРАННЫМ ЧЛЕНОМ  
Академии инженерных наук Российской Федерации

*16 мая 1996 г.*

ПРЕЗИДЕНТ

Академии инженерных наук  
Российской Федерации

ГЛАВНЫЙ УЧЕНЫЙ  
СЕКРЕТАРЬ

Академии инженерных наук  
Российской Федерации



№ 25

Москва, Россия

АКАДЕМИЯ ИНЖЕНЕРНЫХ НАУК  
РОССИЙСКОЙ ФЕДЕРАЦИИ

117810 ГСП-7 Москва В-485  
ул. Профсоюзная, 84/32

тел 333-14-66

факс 333-50-88

*АИИ* № \_\_\_\_\_  
на № \_\_\_\_\_

Dear Dr.-Ing. H.J.Scheel,

We have a pleasure to congratulate you with your election as a foreign member of Academy of Engineering Sciences of Russian Federation.

We appreciate your valuable contributions in the development of materials engineering and technology and hope you will introduce in the engineering sciences further new important contributions.

With all good wishes in your future work and teaching.

President

A.M. Prokhorov

Chief Scientific Secretary

I.A. Shcherbakov





# 학 술 상

Swiss Federal Institute of  
Technology Lausanne  
Dr. Hans J. Scheel

귀하는 본 학회에서 우수한 논문을 발표하시어 학회 발전에  
이바지한 공이 크므로 이에 학술상을 드립니다.

2001년 4월 27일

사단법인 한국결정성장학회  
회 장 오 근 호



## Scientific Award

Dr. Hans J. Scheel  
Swiss Federal Institute of  
Technology Lausanne

This plaque is presented as a token of our appreciation for  
presenting a distinguished paper at the KACG, and greatly  
aiding in the development of our Association.

With affectionate greetings from us,

April 27, 2001

Keun Ho Ahn  
President

The Korean Association of Crystal Growth, Inc.