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Double-diffusive convection during growth of halides

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- **Dr. R. Hopkins, Dr. Robert Maelsky, Westinghouse R&D**

This presentation is a science requirement document for a flight experiment

Double-diffusive convection during growth of halides

Outlines

- **Background on Materials Systems**
  - Heavy metal halides and selenides
  - $PbBr_2$
  - Hg_2Cl_2
- **Science Requirement Document (SRD): Need for microgravity experiment**
- **Bridgman Growth**
  - **Morphological developments during melt growth**
  - Toroidal Instabilities
  - Line defects and Point defects
  - Performance of material
- **Physical Vapor Transport Growth**
  - **Preparation of microgravity experiment**
  - Flight Experiment
  - Characterization of crystals
- **Summary**

We will present examples of Bridgman and PVT growth experiments

AOTF Crystals: leader in producing Efficient EO crystals

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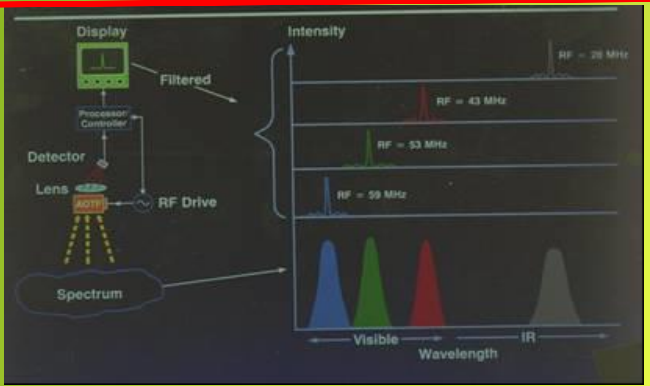
	Acoustic Wave Velocity	Transmission	
AO Crystal	X 10^{-5} cm/sec	Range (um)	Figure of Merit Relative to Si "M_2"
Fused Silica	5.96	0.20 - 4.5	1
$PbMoO_4$	3.63	0.42 - 5.5	23.9
TeO_2	0.620	0.35 - 5.0	695
PbCl2	2.51	0.30 - 20	135
PbBr2	2.30	0.35 - 30	550
Hg_2Cl_2	0.347	0.35 - 20	700
Hg_2Br_2	0.273	0.40 - 30	2600
Hg_2I_2	0.254	0.45 - 40	3200
Tl_3AsSe_3	1.05	1.2 - 16	2800
AgTlSe	1.02	0.80 - 20	1000
TIPSe4	2.00	0.80 - 9.0	1370
Tl3AsS4	2.15	0.60 - 12	416

Examples of the Highest FOM Crystals Which Cover a Very Large Transparency Range

These crystals are key for the hyperspectral imagers for variety of applications



Wavelength filtering

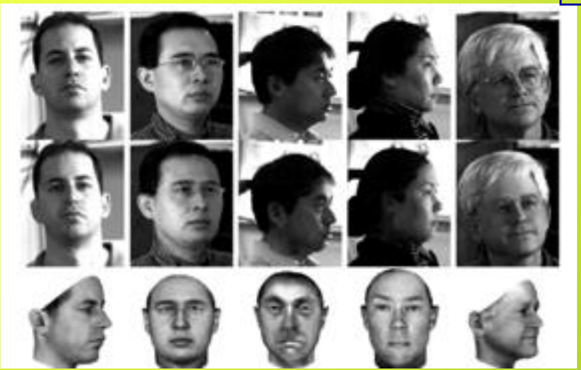
AOTF covering visible to LWIR Range

Target

Red

Blue

Green



To identify the bad guy

AOTFs Can Be Optimized for specific Mission: Face Recognition, Airborne Detection Of Ground Vehicles, Airborne Detection of Trace Gases for UGF Detection & Localization

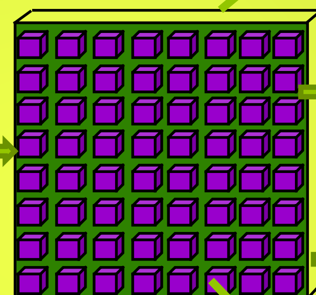
These crystals are suitable for Low cost, large volume multifunctional detectors (γ-ray and MWIR and LWIR)

- Low cost source materials (Avoid rare earth elements)
- Low temperature process
- Large volume production
- Avoid materials which require special handling
  - Hygroscopic
  - Fabrication/special electrode bonding etc

Crystal

Detector

Array



Cost : Success of NaI is good example
Performance: CZT is good example

Cost, quality and timing and multifuctionality approach (Heavy metal halides-Chalcogenides)

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We have grown and fabricated devices from large and small bandgap selenides and halides

- **Selenides (Pure and Doped)**
  - GaSe, $TGaSe_2$
  - PbSe
  - Tl_2Se
  - HgSe
  - ZnSe, ZnS
  - Tl_3AsSe_3, $Tl_3AsSe_{3-x}S_x$, $TlGaSe_2$, $AgGaGe_3Se_8$, $AgGaGe_5Se_{12}$
- **Halides**
- Hg_2Cl_2, Hg_2Br_2, Hg_2I_2 $Hg_2Br_{2-x}I_x$
- $PbCl_2$, $PbBr_2$ and PbI_2
- TlBr, TlI and $TlBr_xI_{1-x}$
- Tl_4HgI_6, $TlPbI_3$ Tl_3PbI_5, Tl_3PbBr_5, Tl_3HgI_5, Tl_3HgI_5



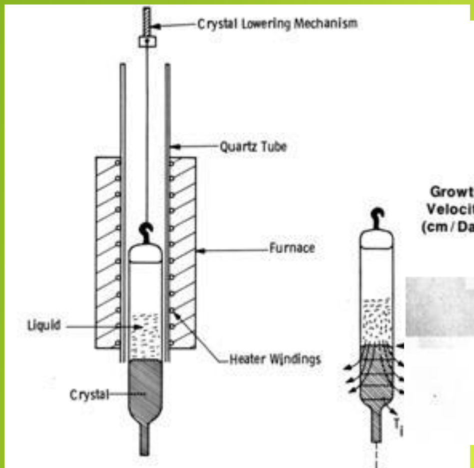


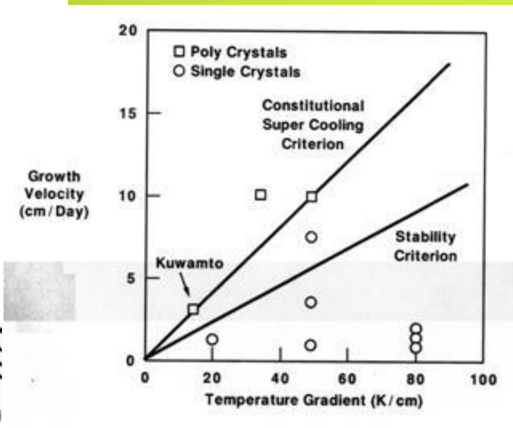


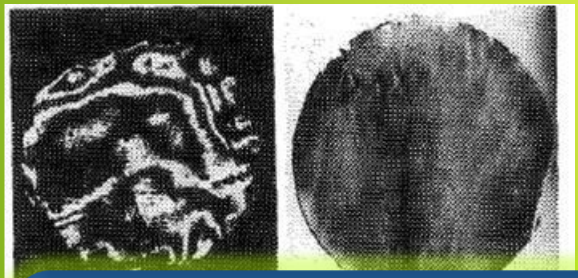


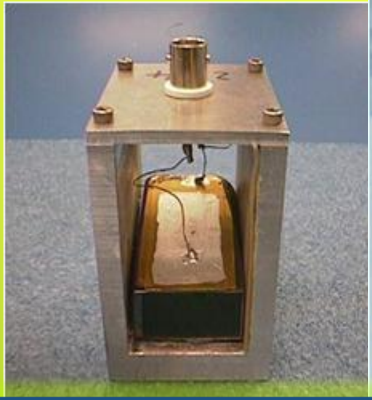


Modeling of convection for the growth is essential when we scale the size









Growth of large crystal is hampered by convection during growt

Double-diffusive convection during growth of halides

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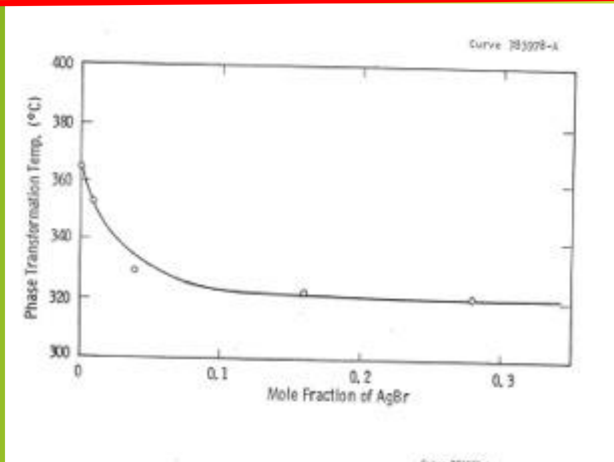
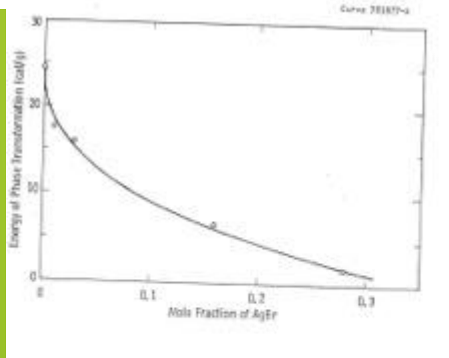
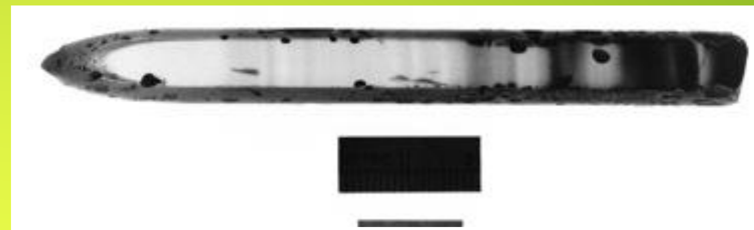
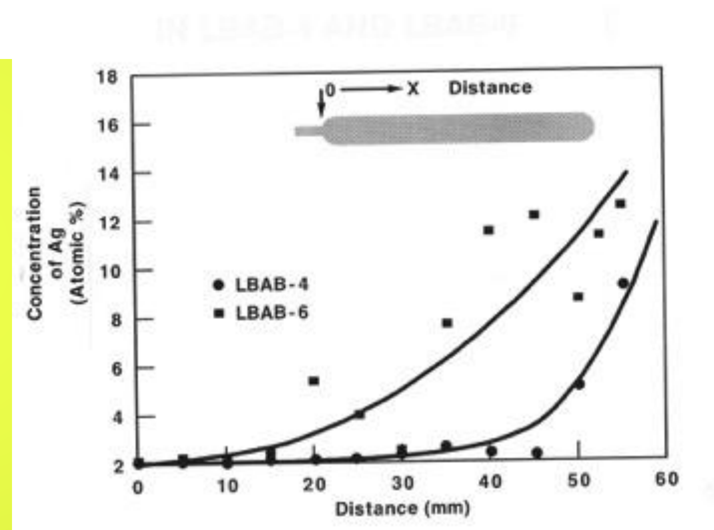
We will present examples of Bridgman and PVT growth experiments

For the direct observation we chose a transparent material system: $PbBr_2$









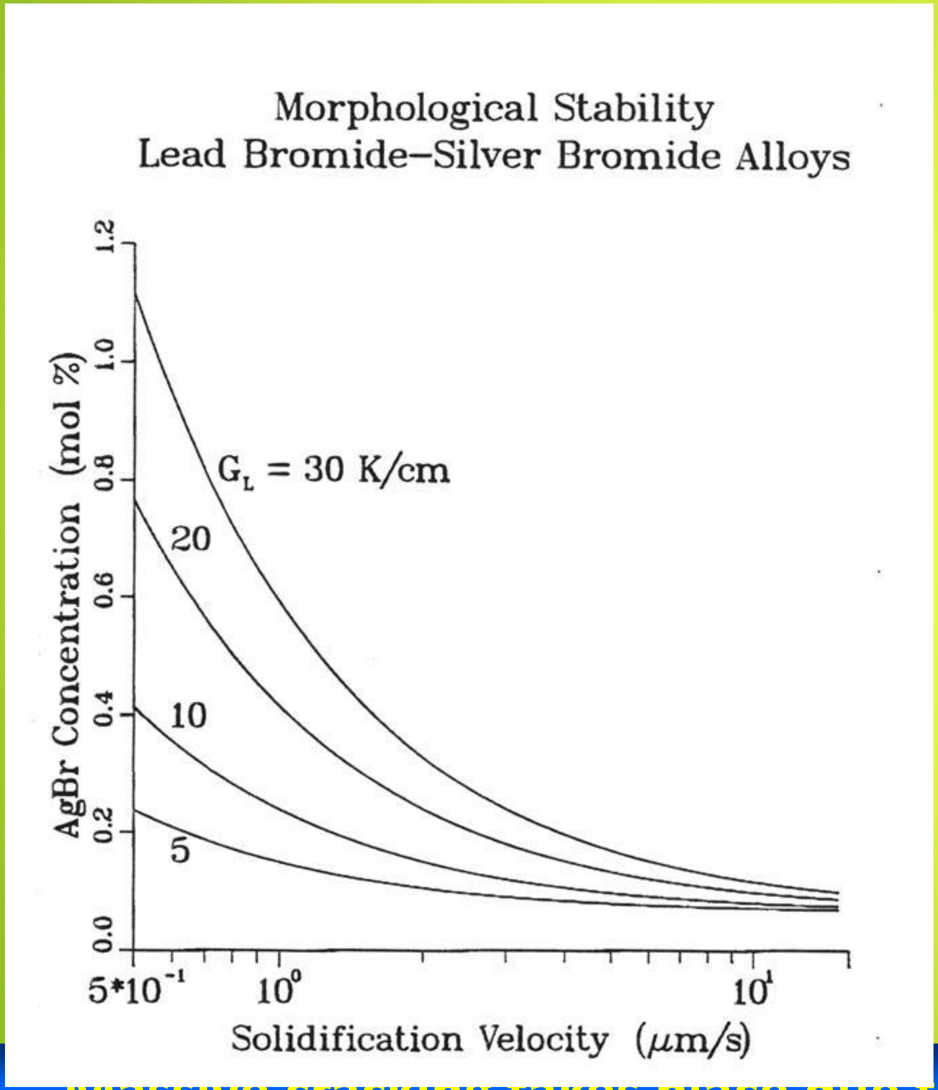
Lead bromide goes through a phase destructive phase transition (Tetragonal to orthorhombic)

Cracking takes place due to phase transition in pure $PbBr_2$

Growth of $PbBr_2$ and PbI_2 crystals was performed in transparent furnaces to control the interfaces

Massive cracking takes place during scale up

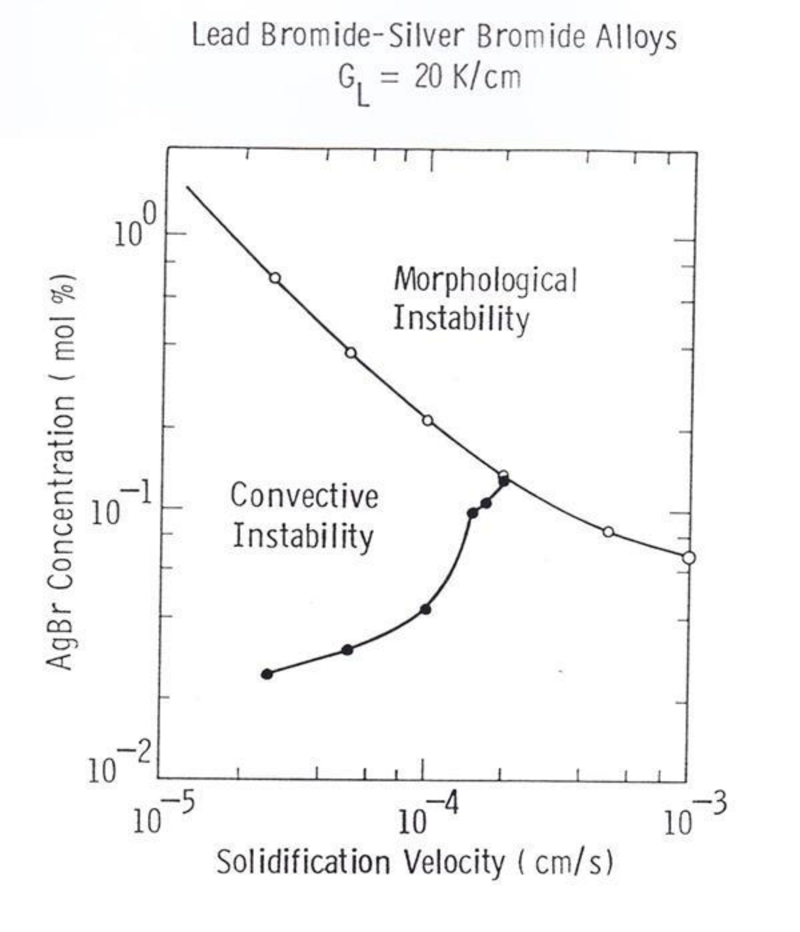
Modeling was performed to evaluate growth velocity for different thermal gradients for planar interfaces

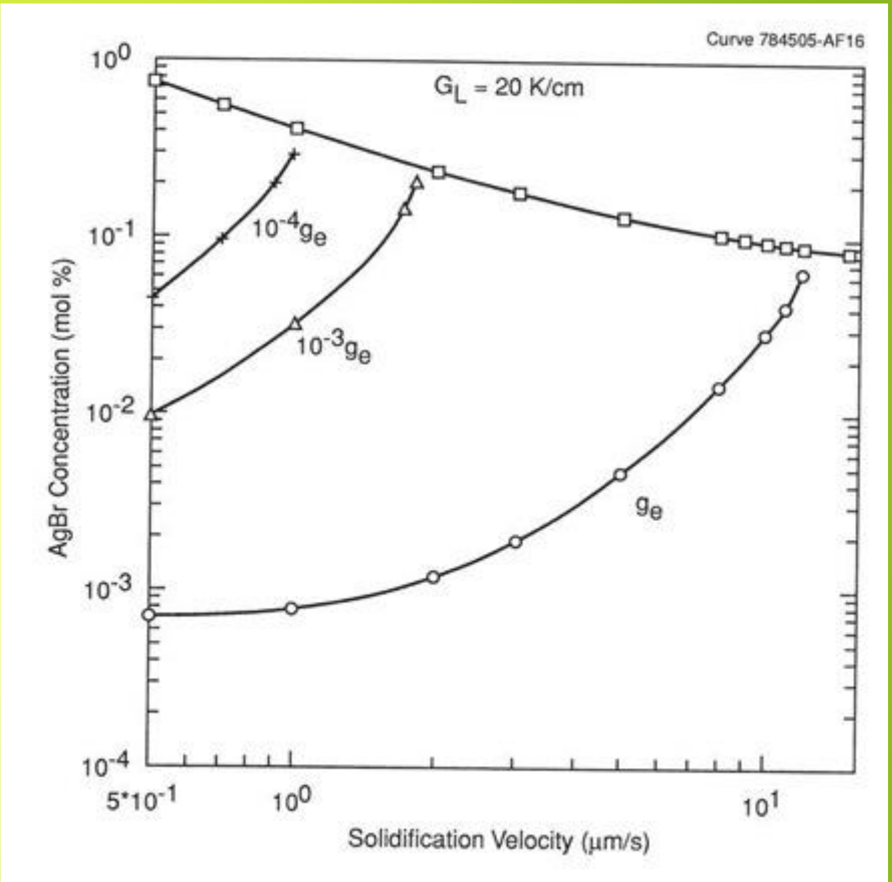


Morphologcal stability limit was determined for Solidification velocity and concentration of dopant

Massive cracking takes place due to phase transition

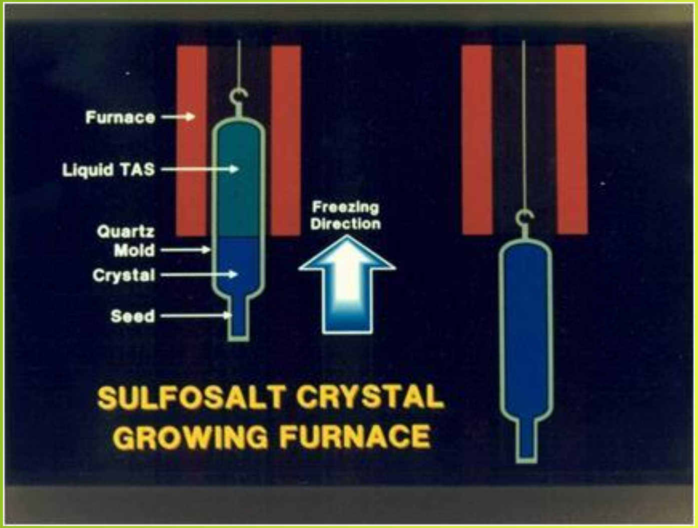
Morphological stability and convective stability were studied for different growth velocities





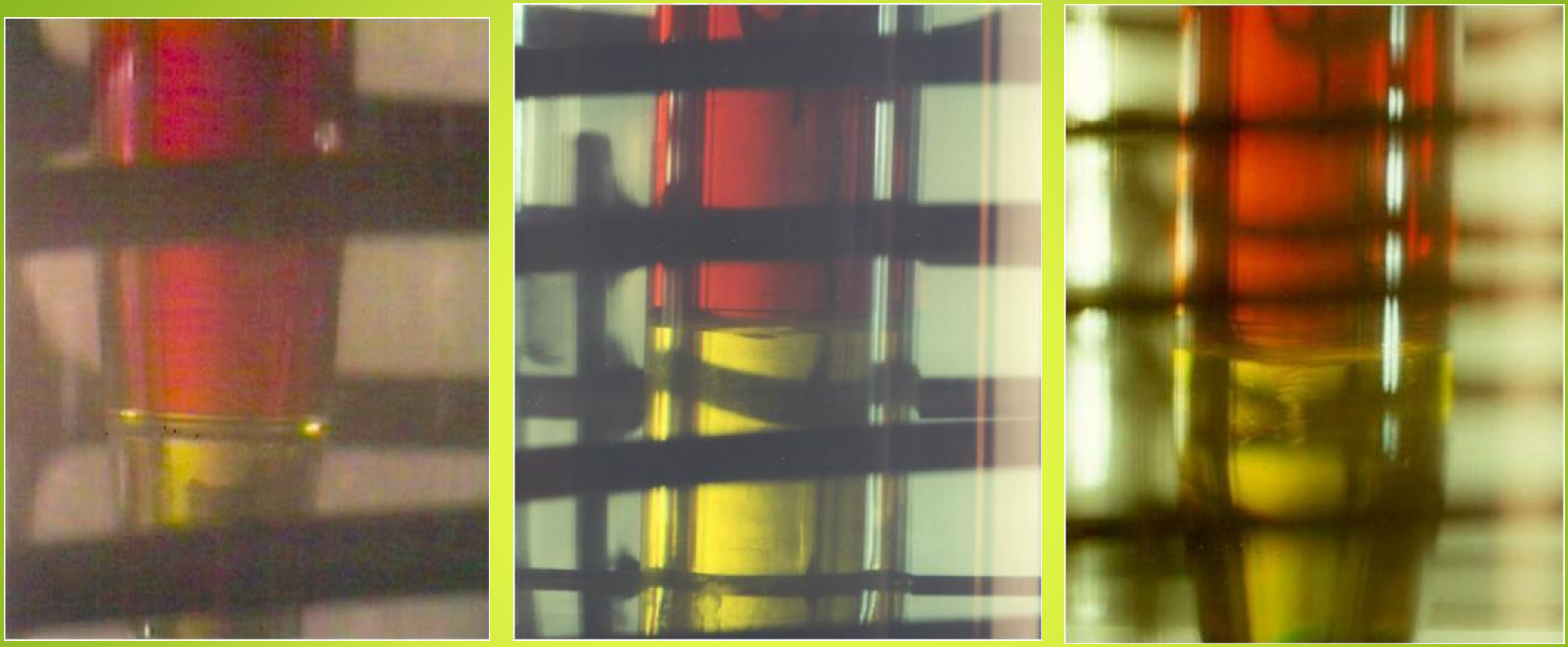
Higher concentration doping was possible for low -g

Growth of crystal was performed in transparent furnaces to control the interfaces



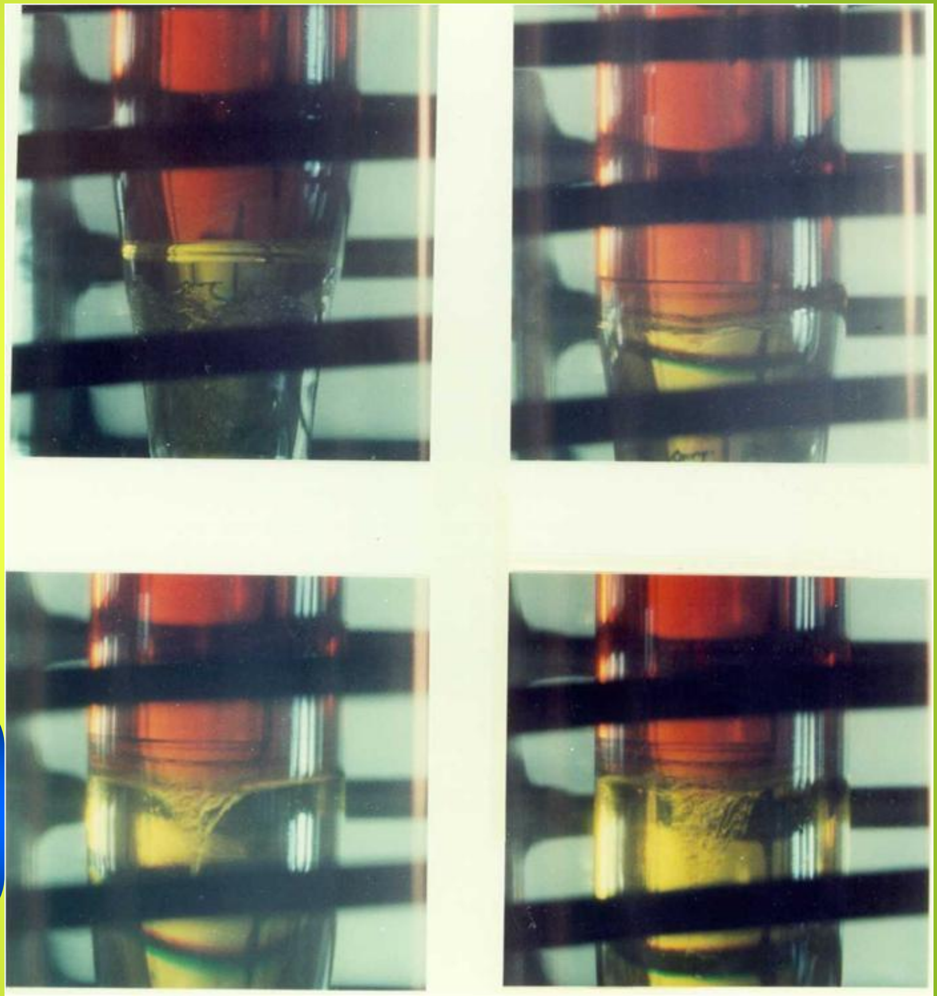
Growth of crystal in transparent furnace

Temperature gradient, growth speed and dopant concentration controls the shape of solid-liquid interface (20K/cm)



As the size of crystal (diameter) increases, convective forces dominate

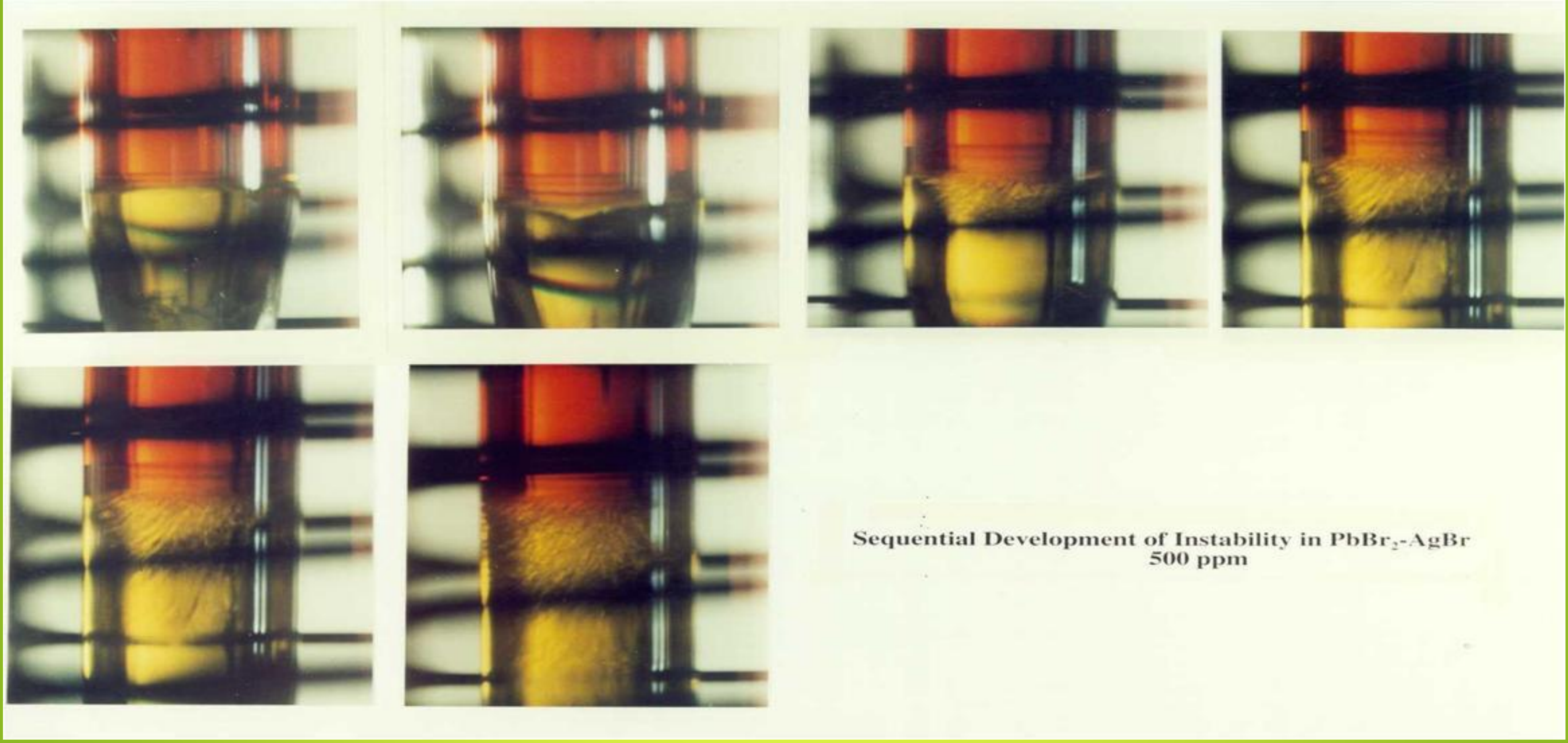
Growth interface and instabilities in lead halides



Sequential development toroidal of instability

Instability is root cause of line and point defects

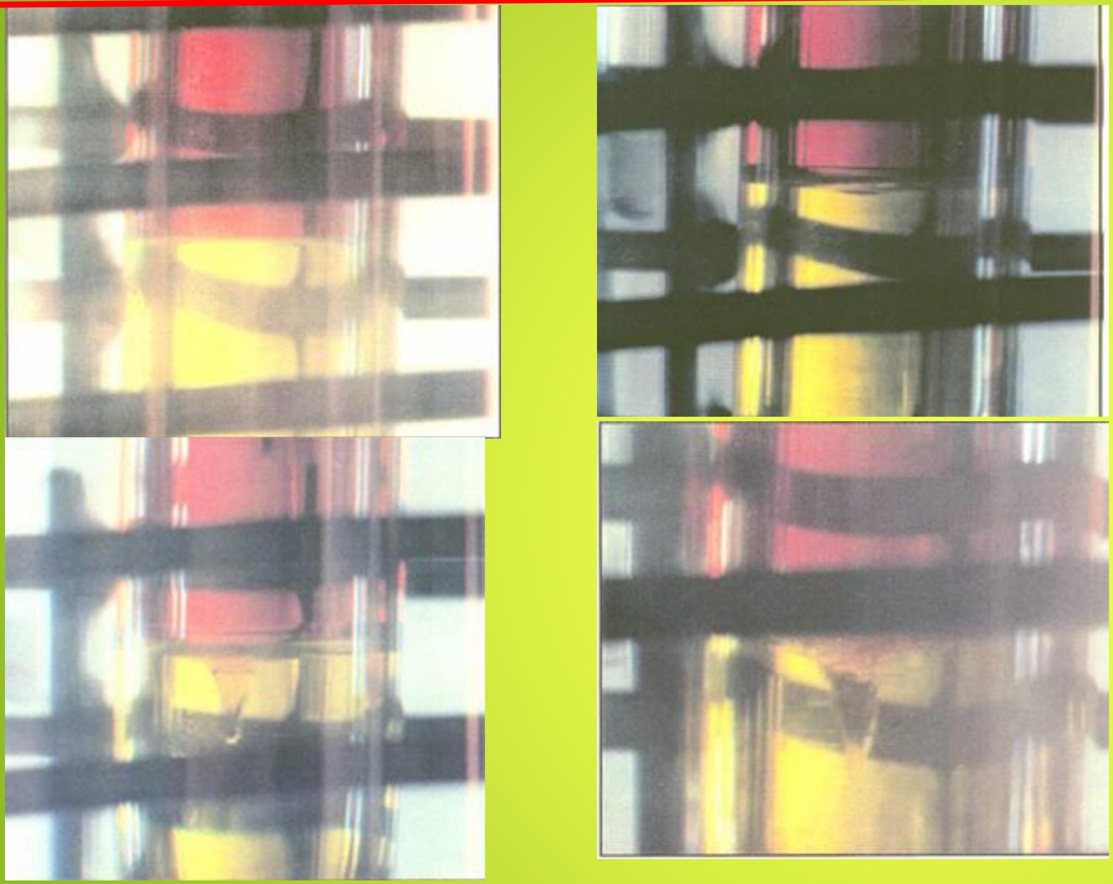
Example of S/L breakdown for 5000ppm doped lead halide; Double diffusive convection plays very important role

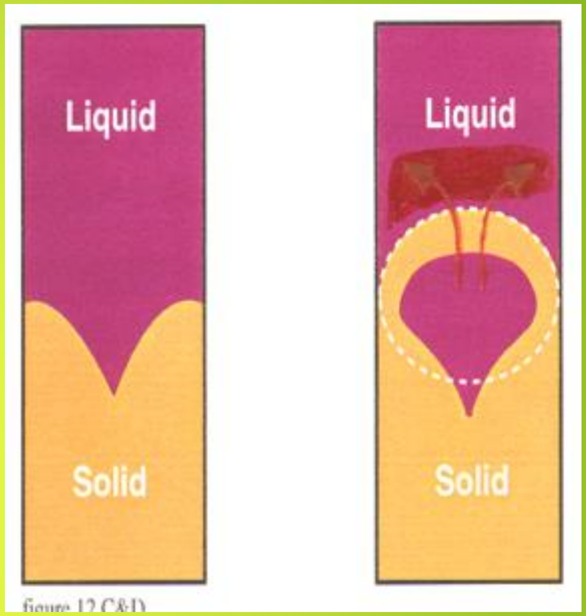


Sequential Development of Instability in $PbBr_2$-AgBr 500 ppm

Interface instabilities in large diameter ampoules turned into dendritic patterns

Role of double diffusive convection was experimentally demonstrated





Torroidal Instability Experimentally Demonstrated

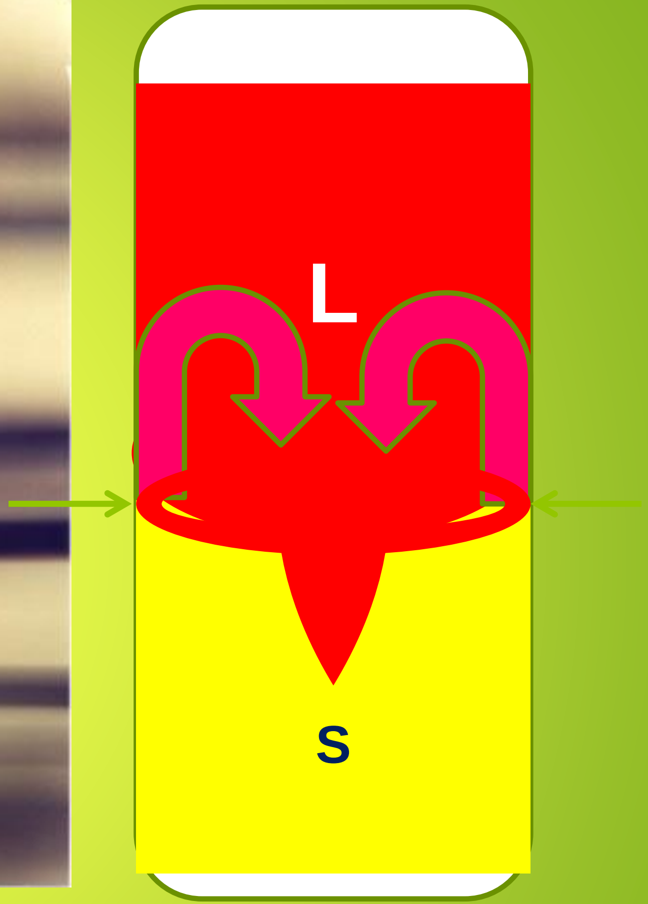
The convective instability can be understood by defining solutal and thermal Rayleigh numbers based on the diffusion length DL/V, namely,

$$Rs = \frac{BC_B g(D_L/V)3}{DL\eta} ,$$

$$Ra = \frac{\gamma G_L g(D_L/V)4}{\kappa L\eta} \qquad (3)$$

where ß is the solutal expansion coefficient, C_B is the silver bromide concentration, D_L is the diffusion coefficient in the melt, η is the kinematic viscosity, γ is the thermal expansion coefficient, and κ is the thermal diffusivity of the melt.

Interface shape during growth



A large line defect and void in the crystal results due to instability. Diameter of the ampoule is 25mm

Growth of crystal in transparent furnace showing line defects and mechanism for torodial instability

1-g grown Crystal and Etchpit density

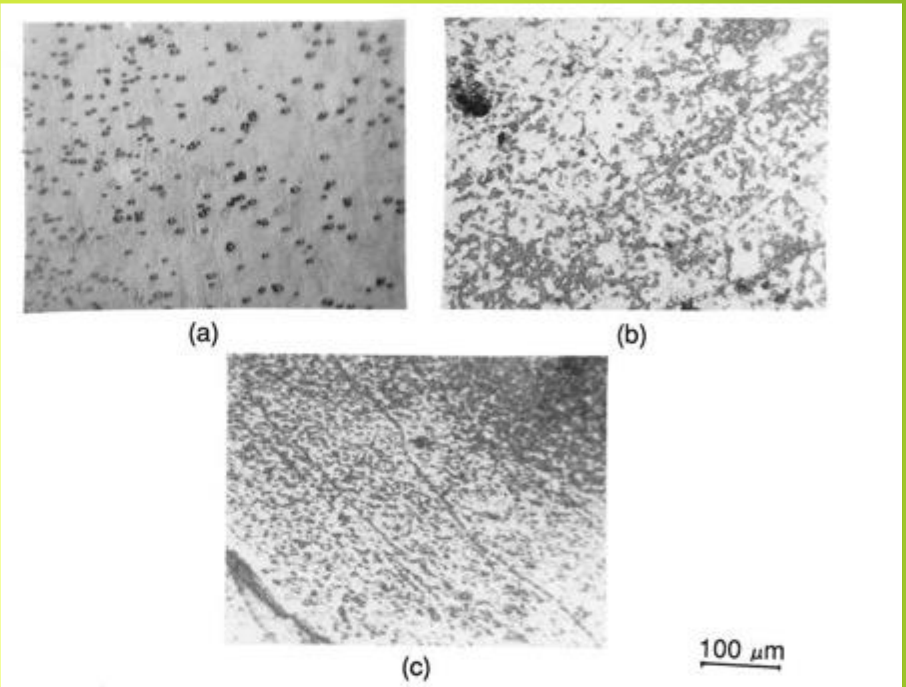
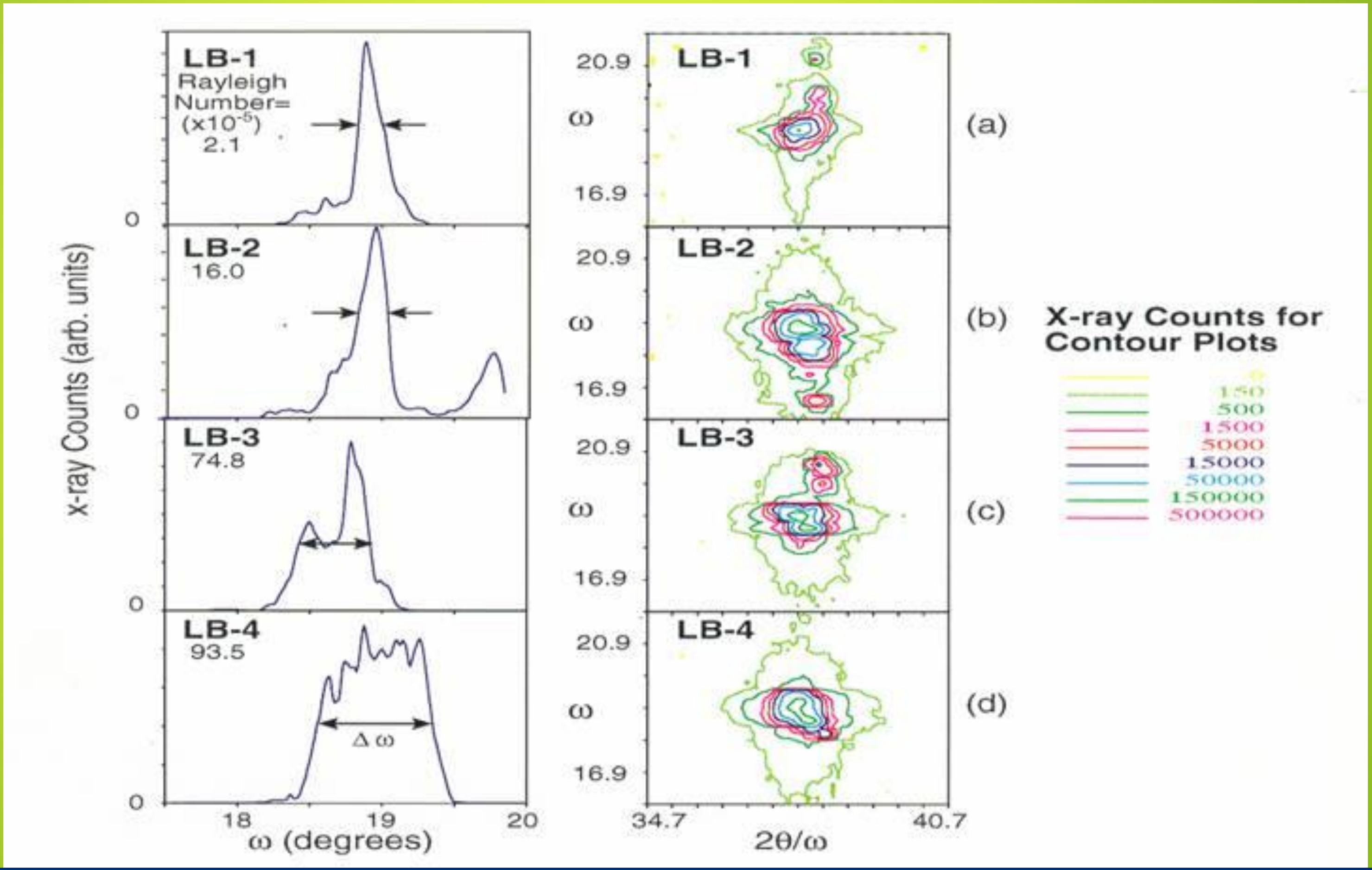


Figure 1. Etchpit density for (a) LBAB-2, (b) LBAB-4 (2 cm from seed end) and (c) LBAB-4 (1.5 cm from tail end) lead bromide crystals showing mosaic spread (ω axis), and spread in lattice constant (2 Θ/ω axis).

Etchpit density showed effect of stresses due to convection

Effect of Thermosolutal effect on the quality of crystal



Quality was function of Rayleigh number indicating effect of convecto-diffusive growth

Some parts of Lead halide –selenide crystals show good quality

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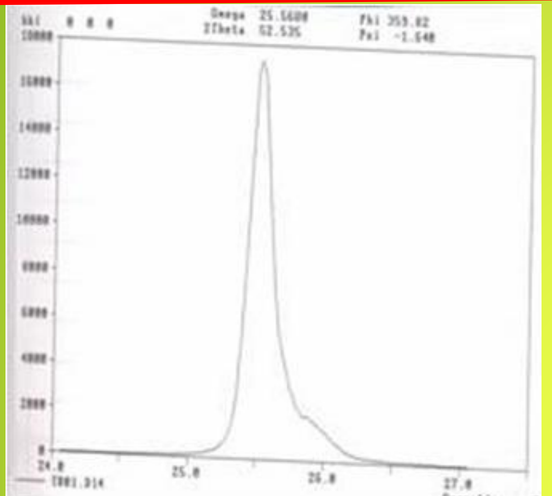
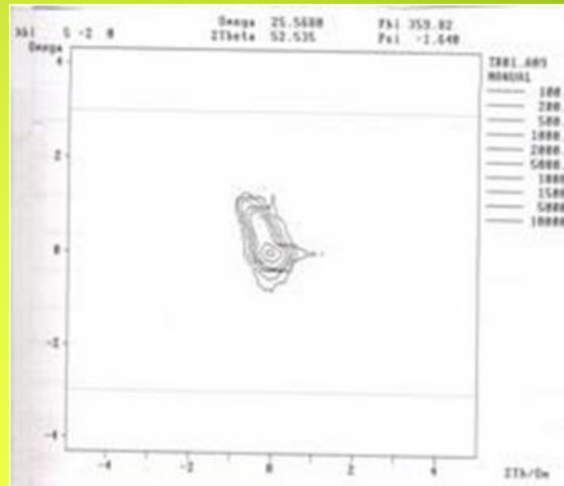
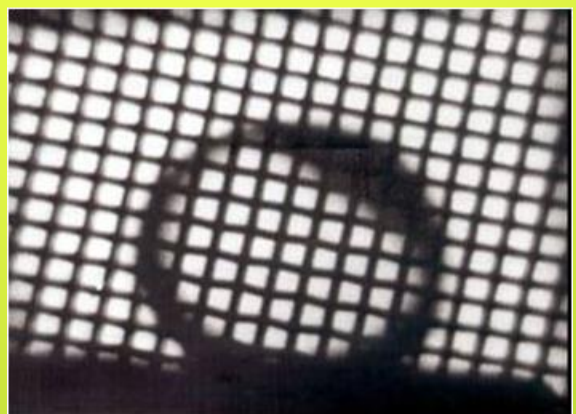




X-ray rocking curve and 2 theta-omega curve for a crystal.



Bulk transparency of crystal with and without wire mesh shows good quality

Crystals showed good quality

Etchpit density for doped crystals

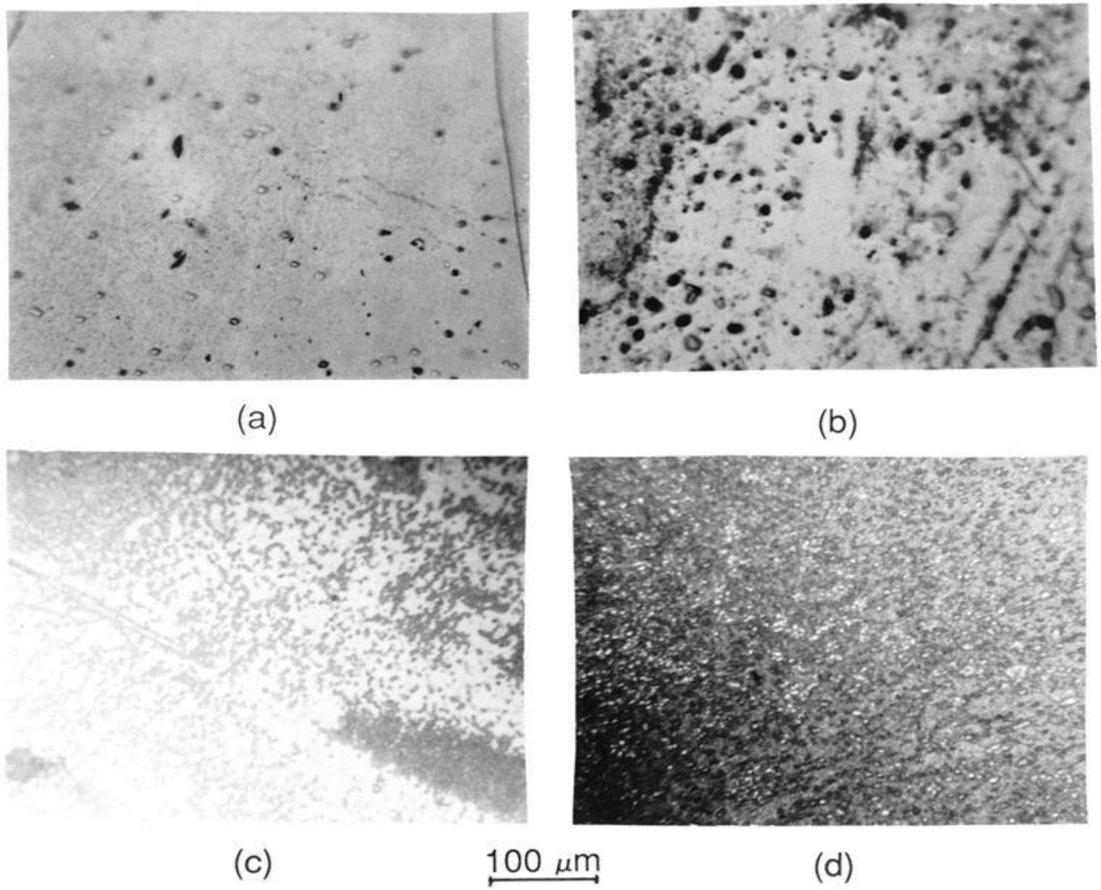


Figure 2. Chemical etchpit for (a) LB-1, (b) LB-2, (c) LB-3 and (d) LB-4 lead bromide crystals showing the increasing defect density.

Etchpit density increased as the convection level (Rs) increased

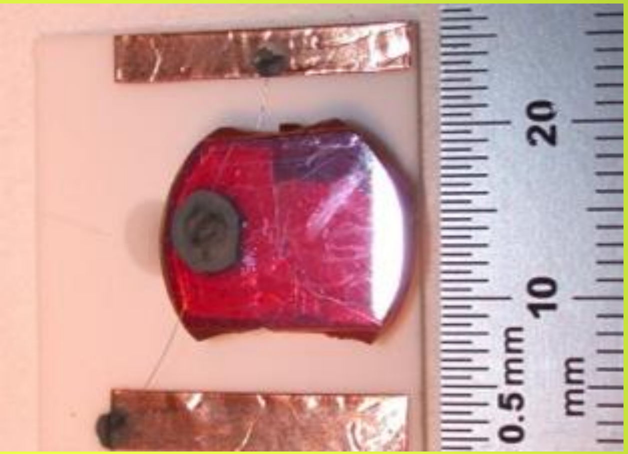
A typical electrical measured resistivity and dielectric constant of halides

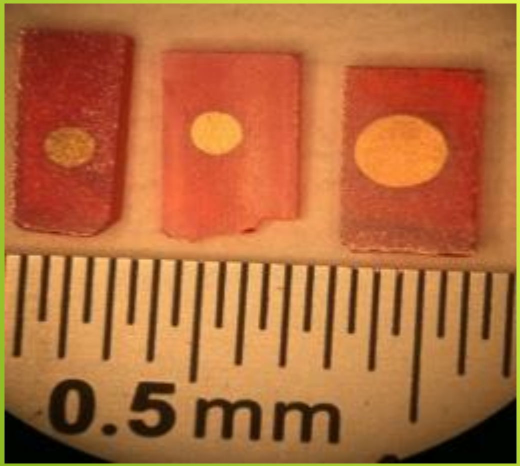
Parameters	PbI_2	$PbBr_2$	$PbI_{2-x}Se_x$
Resistivity (Ω-cm)	$6x\ 10^9$	$5x\ 10^7$	$8x10^{10}$
Dielectric Constant	11.8	30.7	9

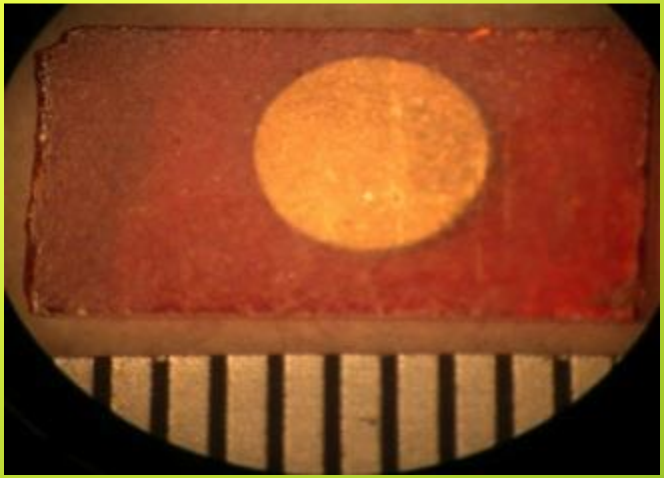
Resistivities are several orders of magnitude lower than HgI_2. But these are very preliminary materials. We are optimzing the materials and processes

Mixed halides had highest resistivity and lowest dielectric constant

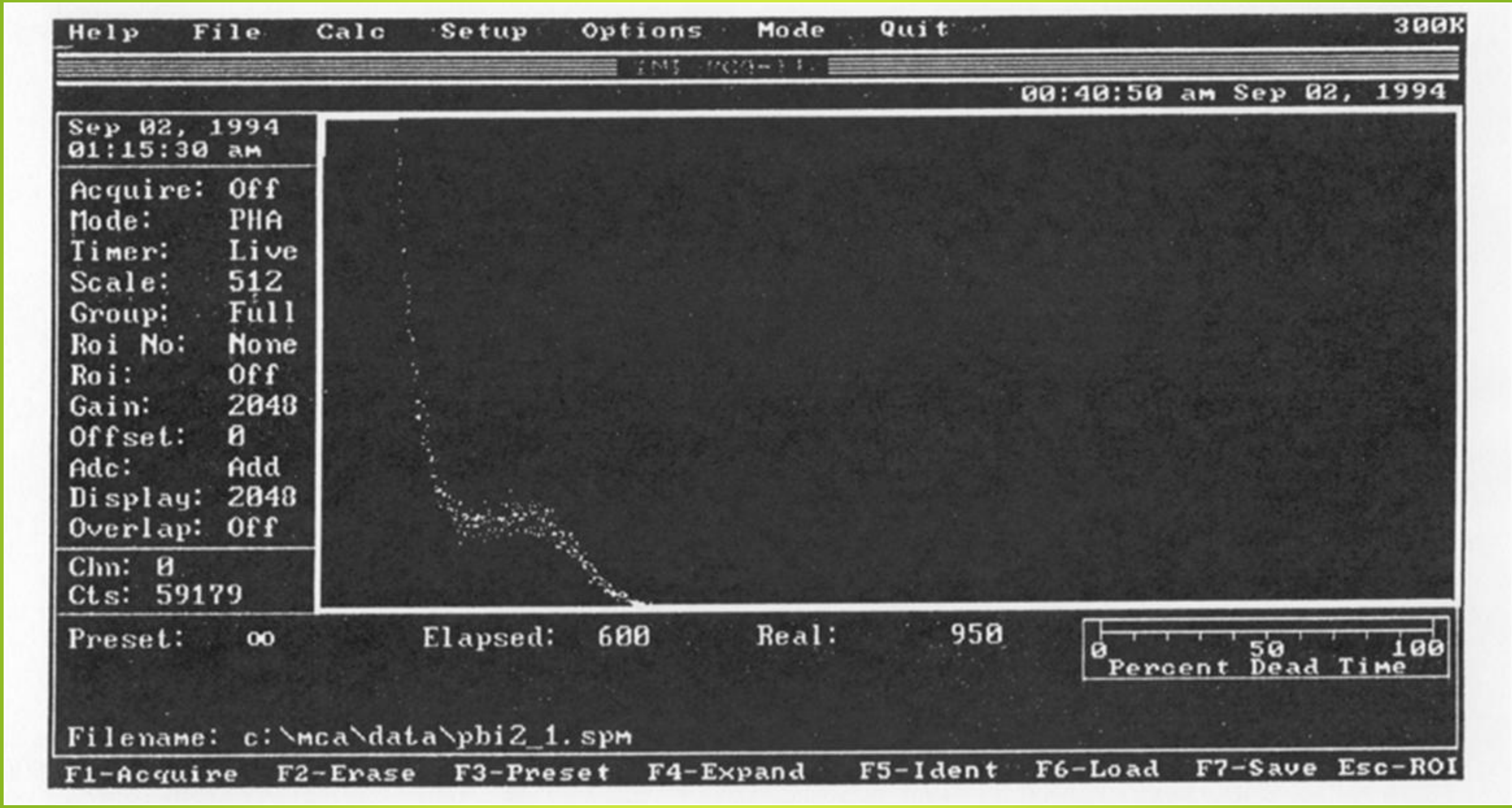
Mixed halides showed good fabricability







Detector of pure salt showing charge collection up to 60 seconds



Charge collection up to 60 seconds

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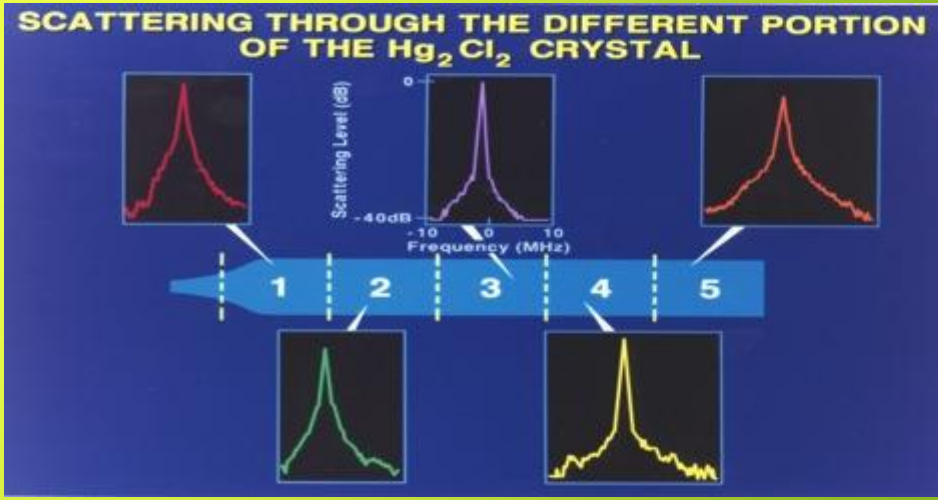
Impurities act as solute and cause solutal convection

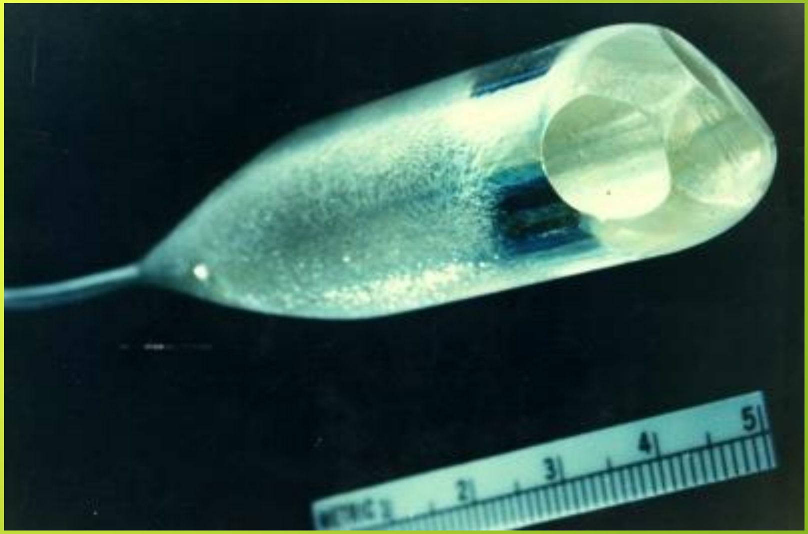


High purity section of crystal showed lowest scattering
Thermosolutal convection cause inhomogeneity

PVT growth: Oriented seeds were used to avoid anisotropic contribution

We used two zone transparent furnaces

Hg_2Cl_2 Crystals with large Natural facets



PVT in Vertical Geometry

The velocity profile across the circular duct is derived by substituting the general expression for shear stress into Newton's law of viscosity and integrating by applying the no-slip condition at the wall. The average velocity is defined as:

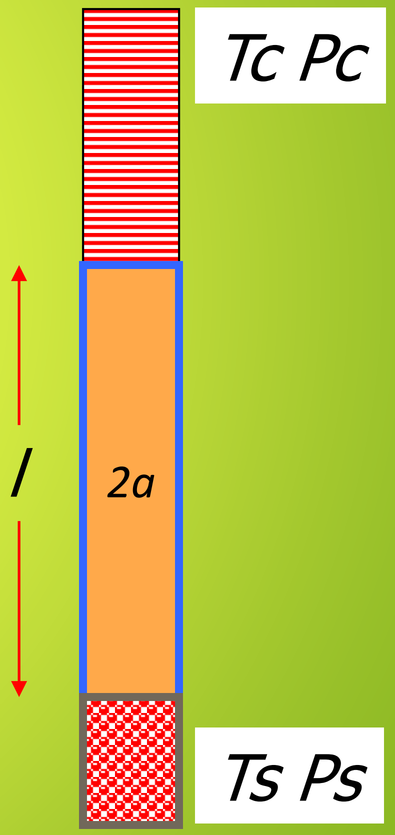
$$\alpha = \frac{\pi a^4}{8\eta l}(Ps - Pe)$$

α = Volume Flow Rate
η = Viscosity

Number of Moles per second through cross section

$$N = \frac{\pi a^4}{8\eta l R}\left(\frac{Ps^2 - Pc^2}{Ts + Tc}\right)$$

where $\Delta P = P_S - P_c$, P_S and P_c are the vapor pressure at the source and crystal interfaces, η is the viscosity, 8η L a result which is Hagen-Poiseuille equation. In spite of the fact that this equation is only applicable to incompressible fluids, one can derive the number of moles, N, flowing each second through the cross sectional area, which is given as:



PVT growth and velocity equation

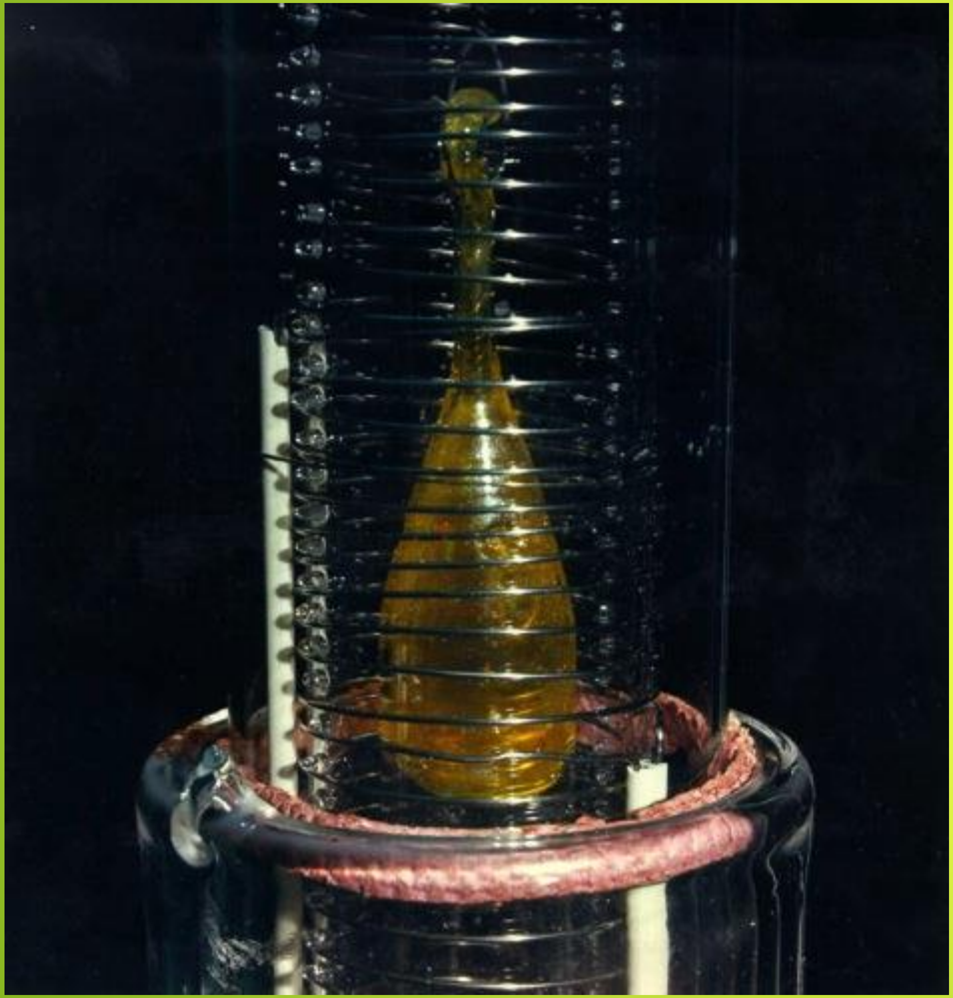
Velocity Equation

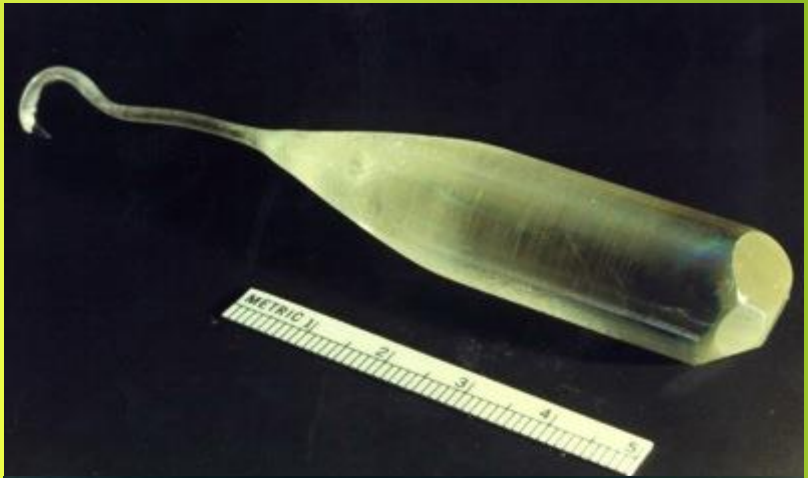
$$V = \frac{9.6a^2M}{\eta l\rho_s}\left(\frac{Ps^2 - Pc^2}{Ts + Tc}\right)$$

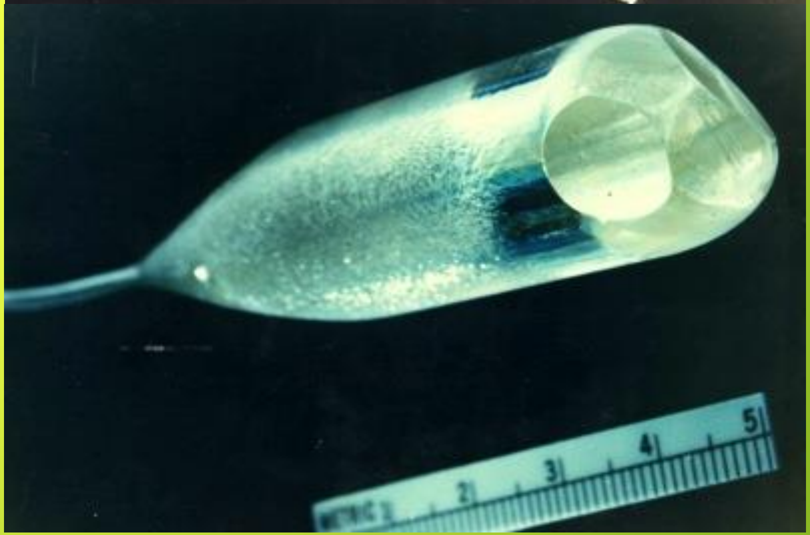
a and *l* in cm
M in g/mole
η in Poise
ρ_s in g/cm^3
Pc and Ps in Torr
Tc and Ts in K

A growth rate higher than 5 cm/day was predicted.

Hg_2Cl_2 Crystals with favorable properties for detectors







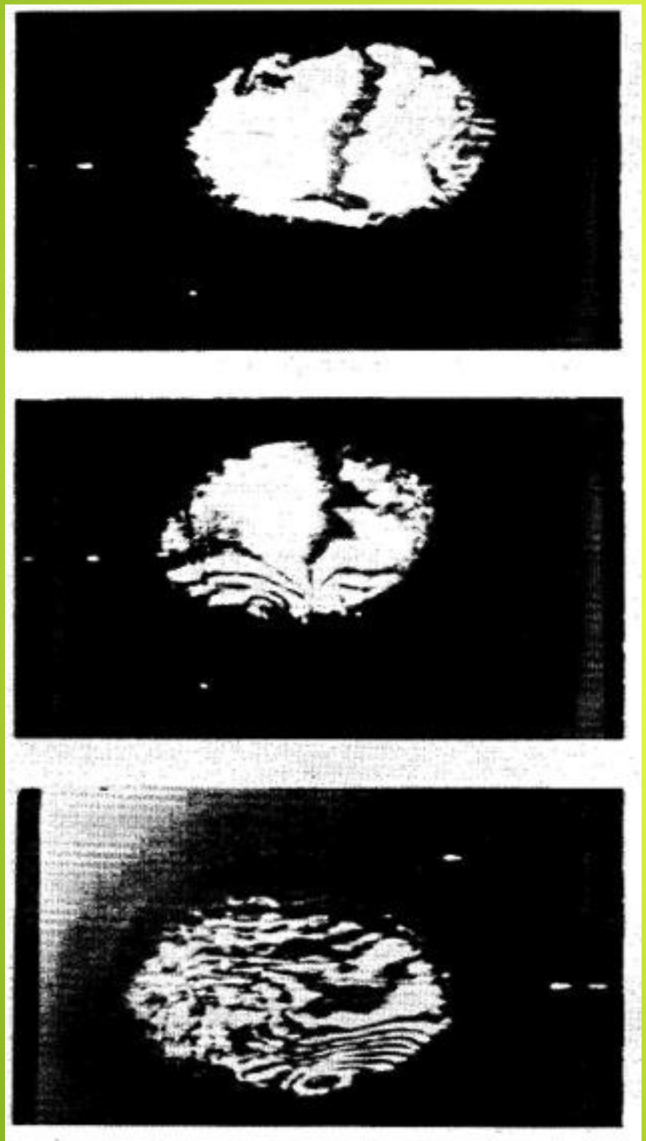
Heavy metal halides were use for 0.3 to 30μm region

We have in-house capabilities for growth of crystal, fabrication, design and system insertion.

Large crystals of Hg_2Cl_2 and Hg_2Br_2

has excellent in-house capability for crystal growth, design, cutting, polishing, AR coating, fabrication, and system insertion.

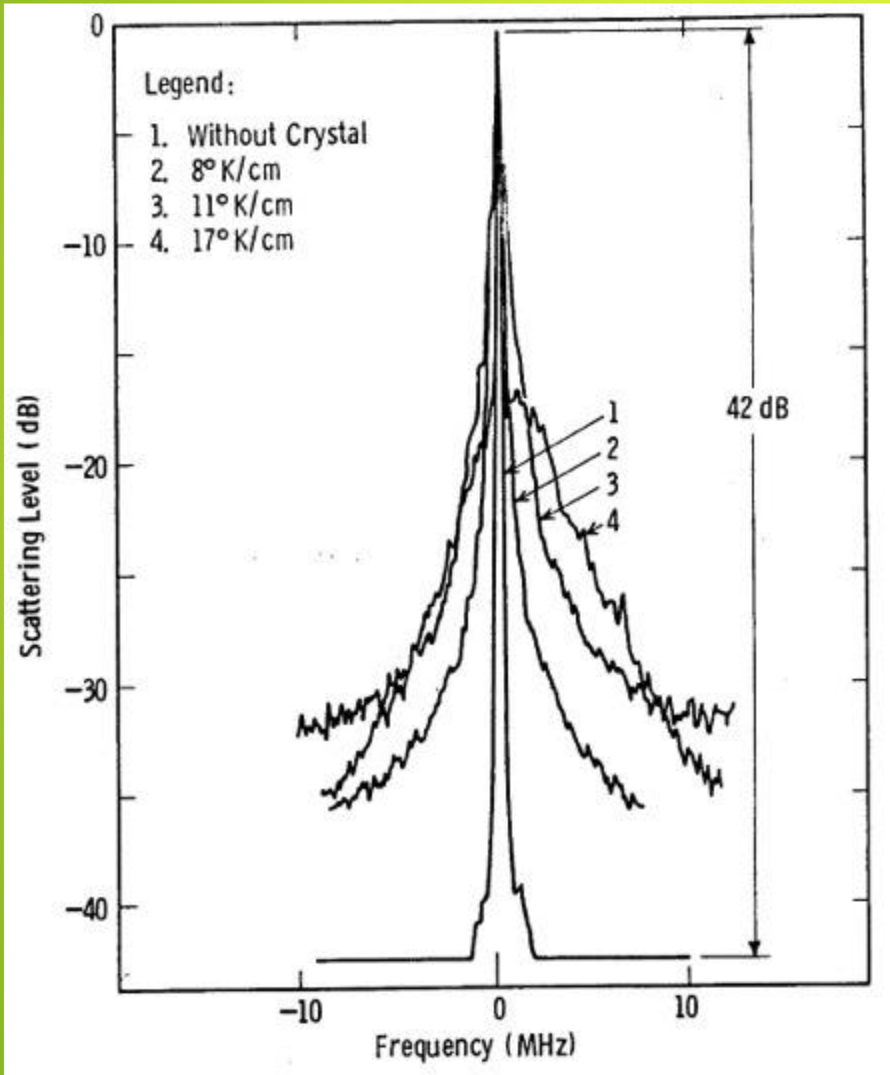
Microgravity Experiment to Grow HgCl Crystals by PVT Method



Birefringence Interferograms for Crystals grown in 1-g

- Birefringence Interferograms for crystals grown at Raleigh numbers (a) 4.55x10^{-2}, (b) 6.25x10^{-2} and © 9.66x10^{-2}.
- The birefringence Interferograms show deteriorating crystal quality with increasing Rayleigh number

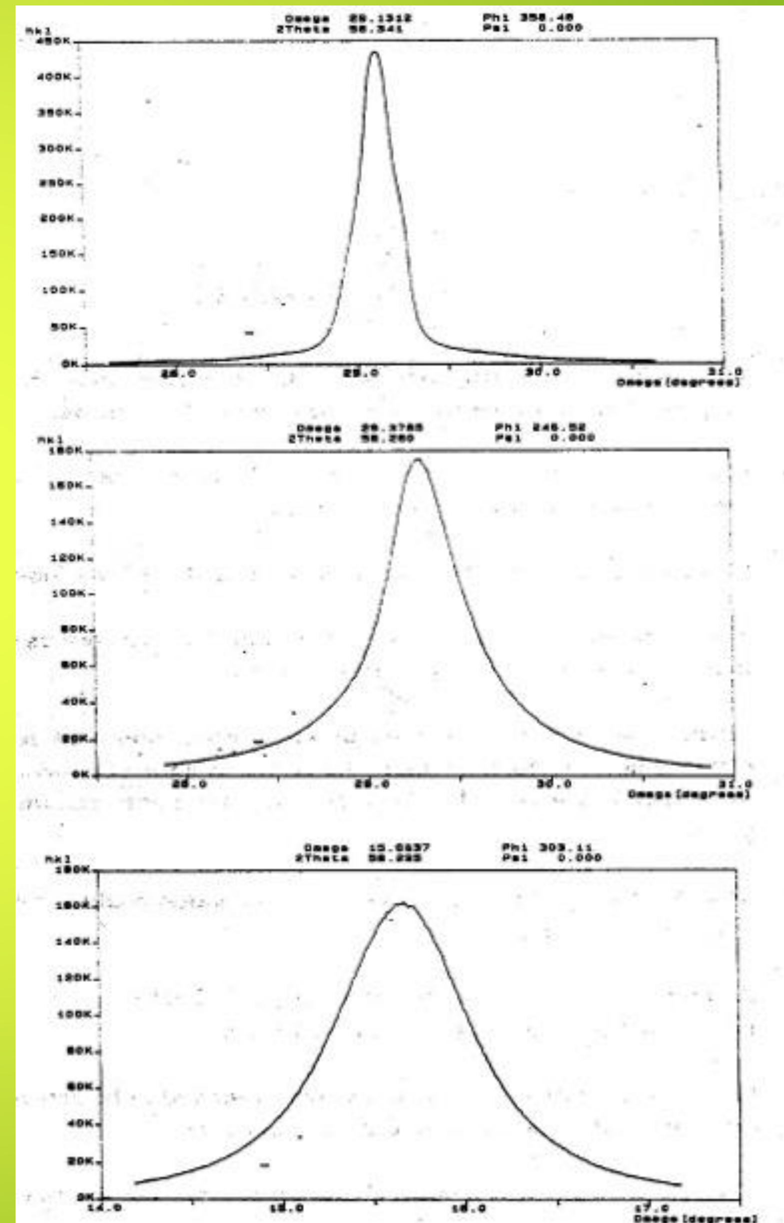
Effect of convective levels on scattering



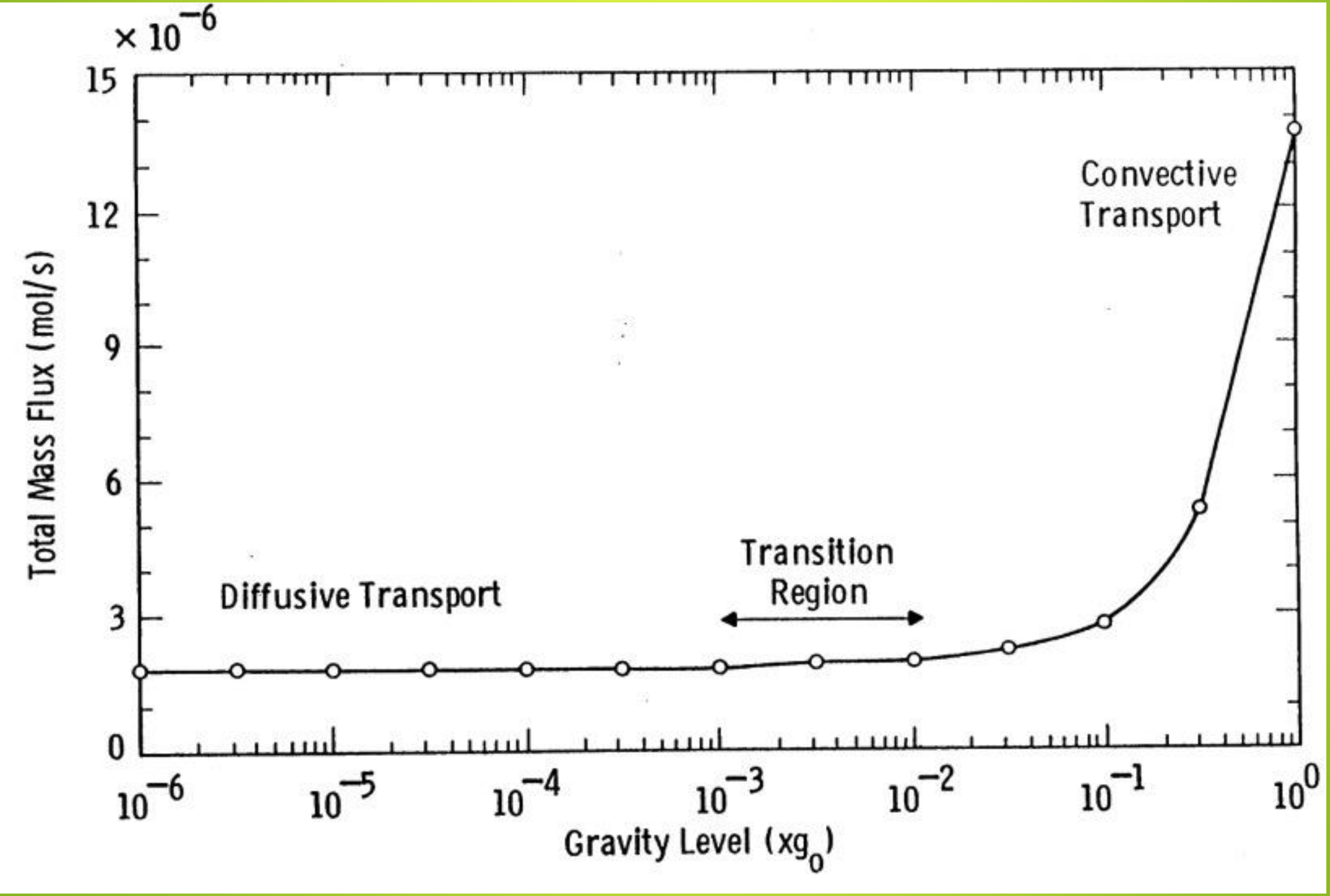
- Scattering for crystals grown at Rayleigh numbers (a) 4.55×10^{-2}, (b) 6.25×10^{-2} and © 9.66×10^{-2}

- The scattering curve 1 is laser beam without crystal

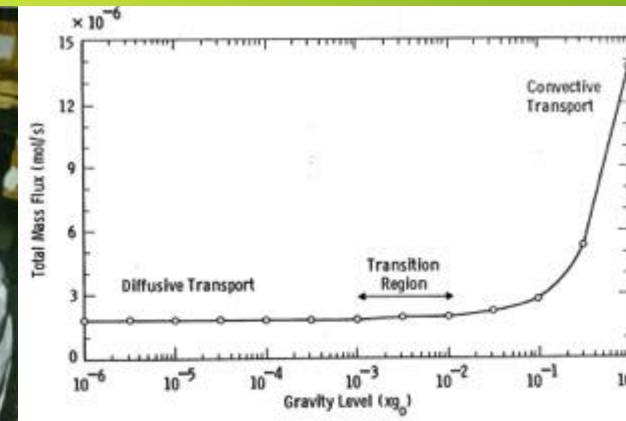
X-Ray Rocking Curve and Bulk Transparency of a Crystal Grown in 1-g

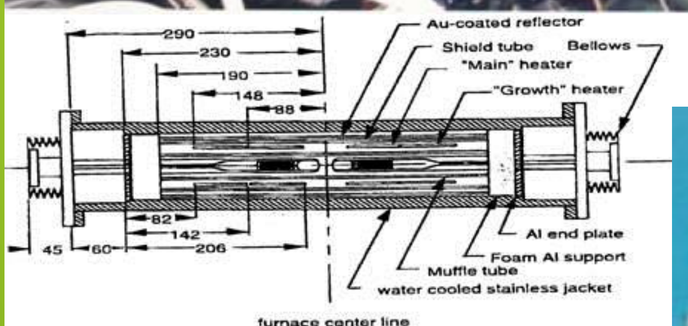


Transport Region for HgCl as the Function of Gravity Level



Microgravity experiments required several days for training of atranauts and space load scientists





Detached growth was observed for the first time in space and in 1-g

Seeded Growth Ampoules and temperature profile for microgravity experiment

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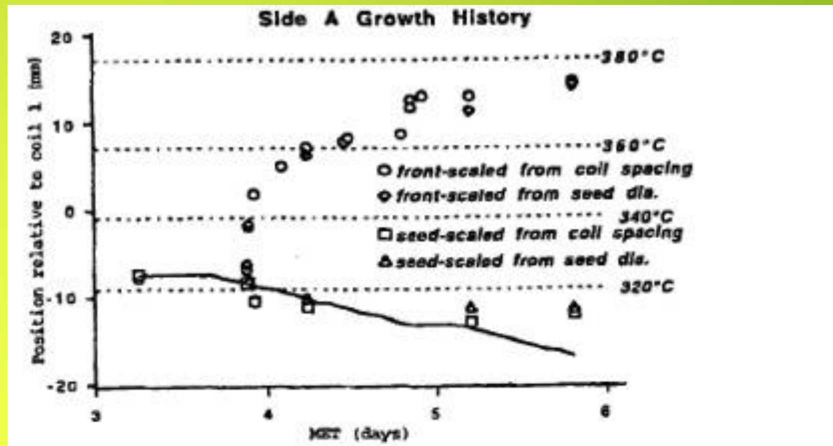


Fig. 4a. Growth history for the A-side crystal. The solid line is the position of the seed inferred from the shaft encoder. Note that the last data points have not been corrected for parallax and are probably too high by several mm.

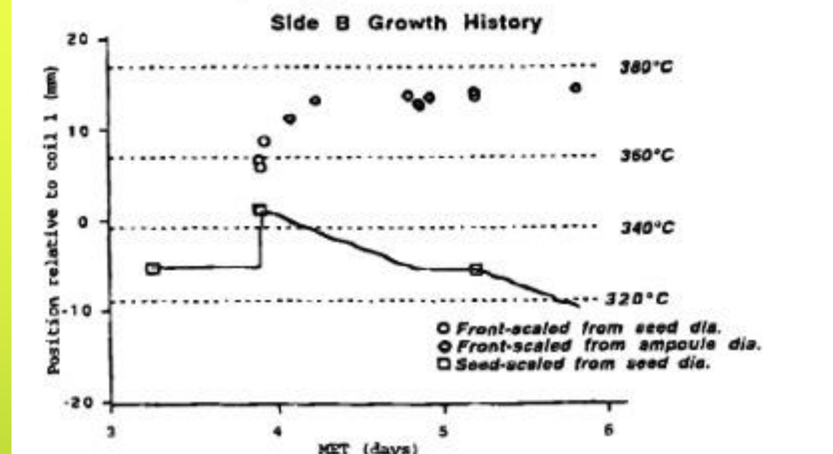


Fig. 4b. Growth history for the B-side crystal. The solid line is the position of the seed inferred from the shaft encoder.

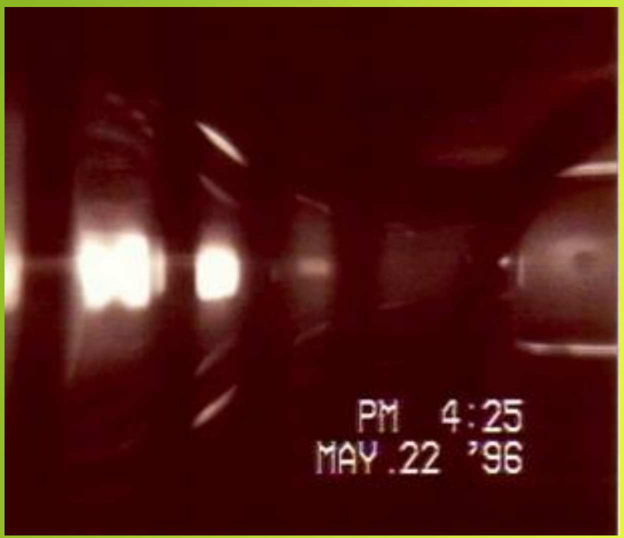
Morphology of growing crystals

Growth Interface of Crystal A in Space at Different Time

Microgravity Experiment to Grow HgCl Crystals by PVT Method

Growth Interface of Crystal on A side

Microgravity Experiment to Grow HgCl Crystals by PVT Method



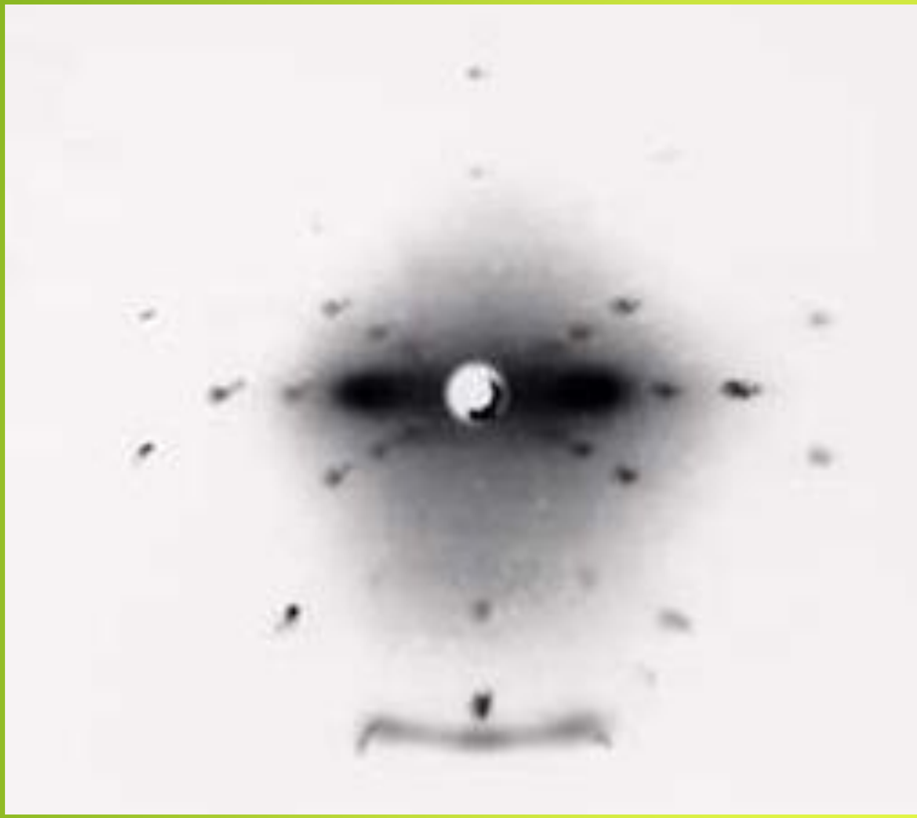
Growth Interface of Crystal B in Space at Different Time

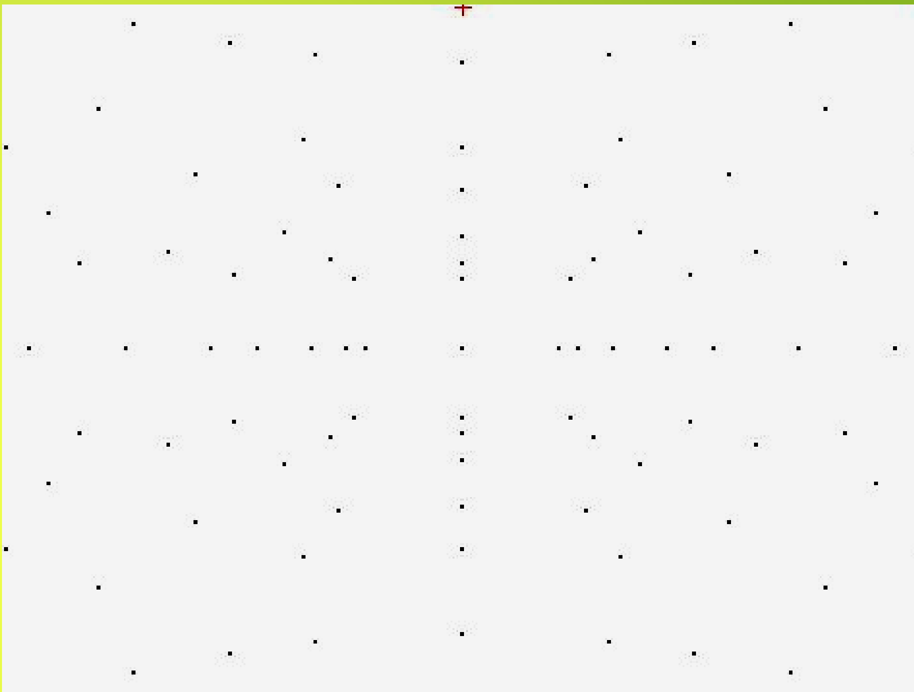
Microgravity Experiment to Grow HgCl Crystals by PVT Method

Growth Interface of B crystal in Space

Two HgCl Crystals Grown in Space

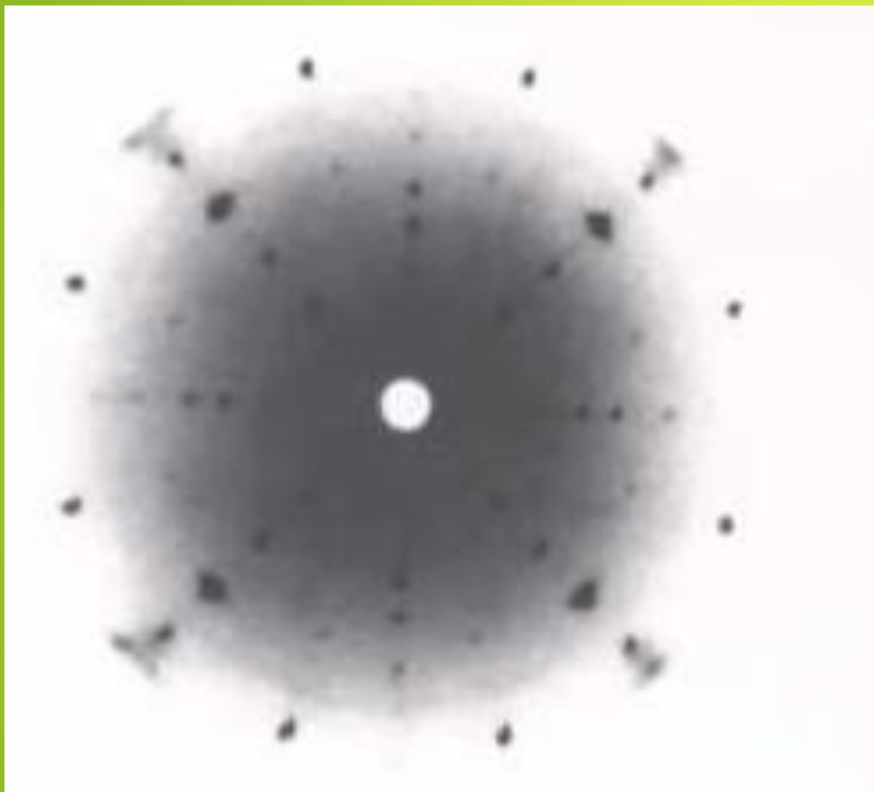
Experimental and theoretically constructed <110> orientation of Hg_2Cl_2 crystal

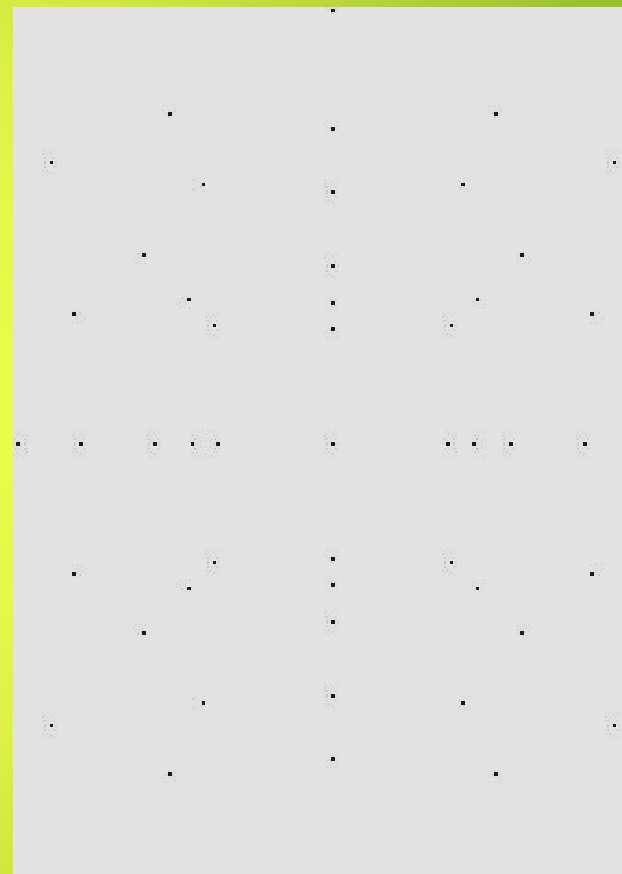




- ***This***

Experimental and theoretically constructed <001> orientation of Hg_2Cl_2





This is for HgCl tetragonal crystal

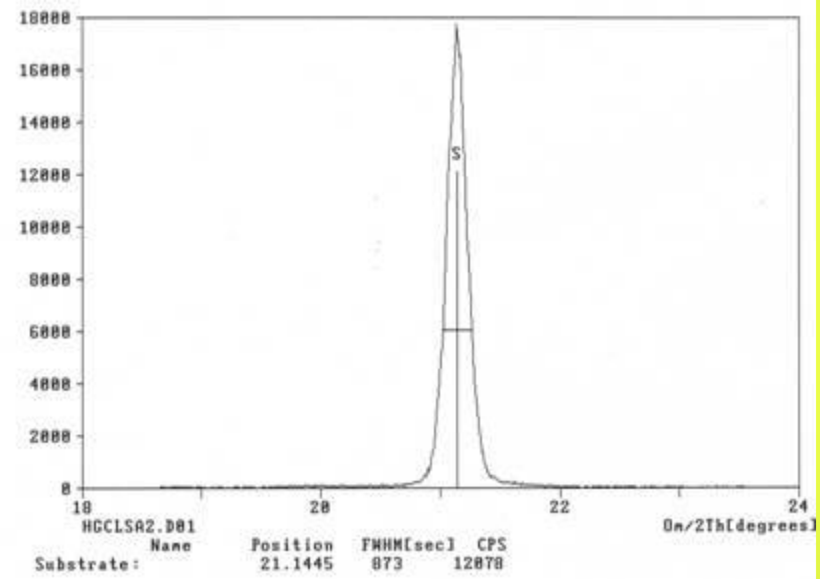
Bulk Transparency of Crystal A and B with and without wire mesh

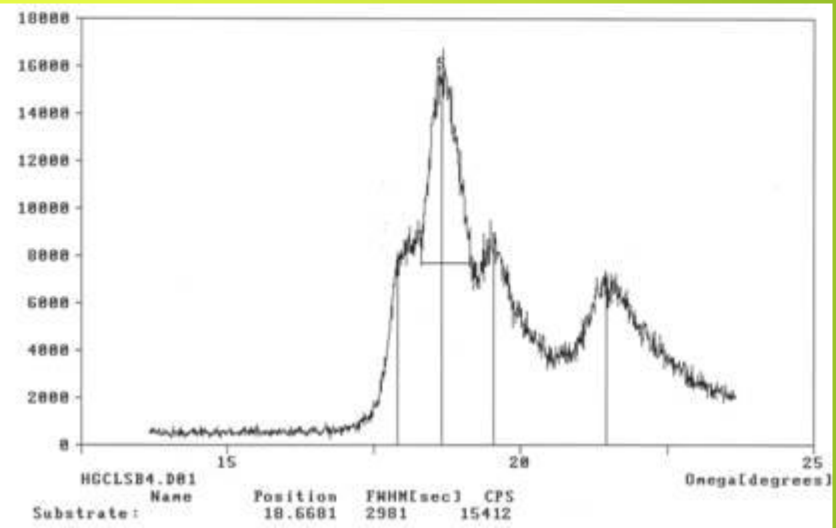
A

B

Microgravity Experiment to Grow HgCl Crystals by PVT Method

Rocking Curve for crystal which was not crack showed good quality





Summary: Sound ground base experiment is essential before the microgravity experiment

- **Bridgman Growth**
- Heavy metal halides are excellent Acousto-optic materials
- Direct observations were taken during solidification
- Interface showed toroidal instability in presence of AgBr impurities
- A quantitative correlation was established between convection and quality of crystals for Bridgman growth (SRD)

- **Physical Vapor Transport Growth**
- Microgravity PVT experiment was carried out in STS-77 in Spacehab-04 to grow mercurous chloride crystals
- Two crystals were grown with translation rates of 5 mm/day and 9 mm/day
- Crystals did not follow [110] orientation in Space.
- Crystals grew faster in the center of the ampoule compared to edges.
- Furnace shut down occurred due to another payload purges.
- Crystals quenched with a very fast cooling rate.
- Quality of small crystals (taken from uncracked portion) were very much superior than 1-g grown crystals

Materials are key for the performance of systems

No one wants to fail. Everyone wants society, love and appreciation

Climax and anticlimax are part of the life

Help me, I will see everything what you have seen, but I will think in a way you never did, and I will patent it and publish papers

Guide me by coaching, I will learn from my own mistakes

No one wants to fail, everyone needs appreciation and little help to achieve success

Thank you very much for your attention