

# Chalcogenide Glass for Active and Passive Mid-IR Applications

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# Report Documentation Page

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# Outline

- Background
- Purification and synthesis
- Optical fibre development
- Active devices in the mid-IR
- Concluding remarks

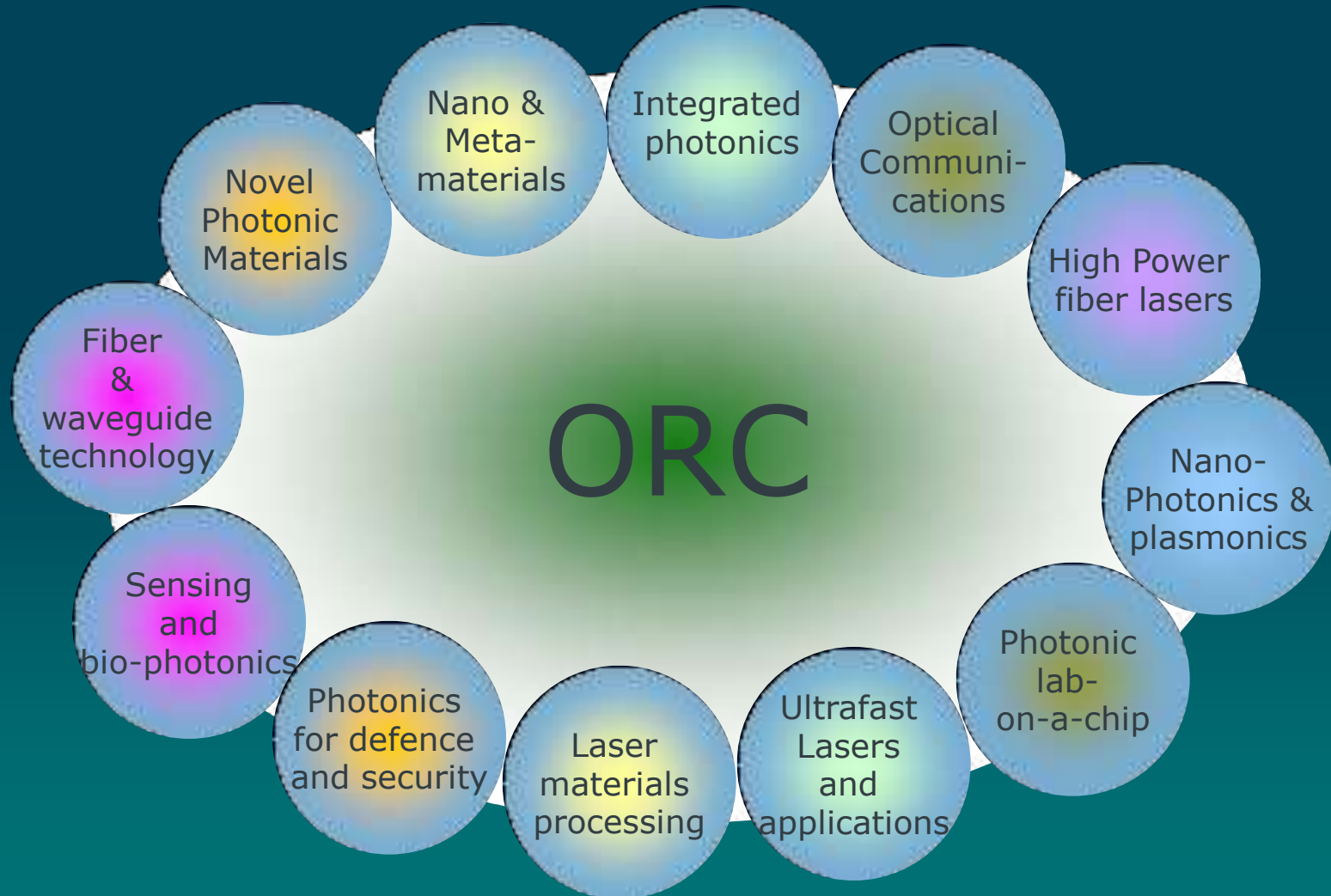


## Optoelectronics Research Centre

- 40 year history beginning from ground breaking work in optical fibers
- Now the largest group in UK (170 staff / PhD students, 65 labs)
- Generates ~50% of our Universities Intellectual Property
- Extensive international industrial and University links
- A worldwide alumni of 600 staff many in senior positions
- A photonics cluster of 11 companies
- 270 Publications/11 Patents per year
- 50 Invited / Plenary talks per year
- Staff includes 3 Fellows of the Royal Society

# Primary Research Areas

UNIVERSITY OF  
**Southampton**  
Optoelectronics  
Research Centre



# Purification & Synthesis



- Raw materials
- Reactive gas conversion
- Chemical vapour deposition

# The Chalcogenides

## What is a Chalcogenide?

- From Greek *sulphur-loving* for elements that frequently bond to sulphur
- Seen in various forms: crystalline, single crystal, quantum dots, phosphors, ceramics

## Typical Amorphous Compositions

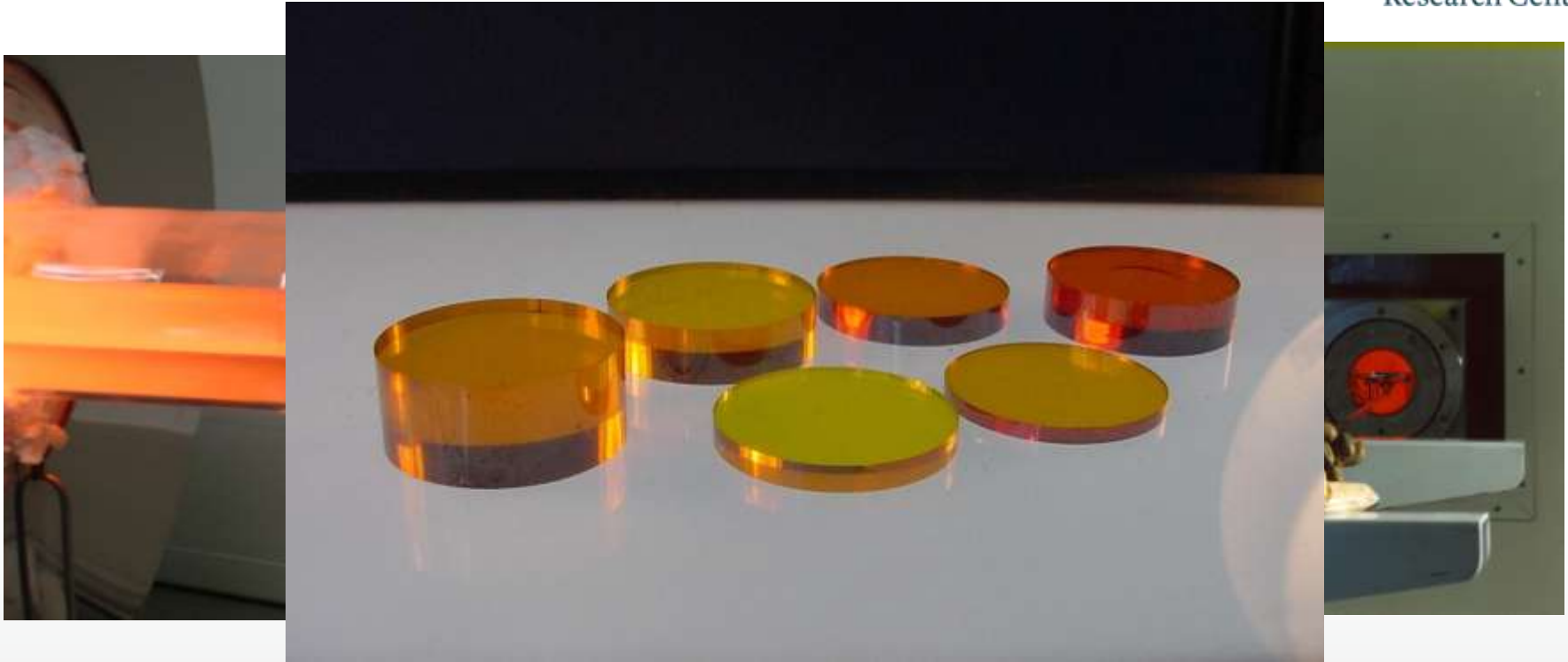
- As-S, As-S-Se, Ge-Sb-Te
- Predominately As or Se based (toxic!)

## ORC Research Focussed On

- Gallium Lanthanum Sulphides (non-toxic)
- Germanium Sulphides (non-toxic)
- Capability to melt any glass composition exists



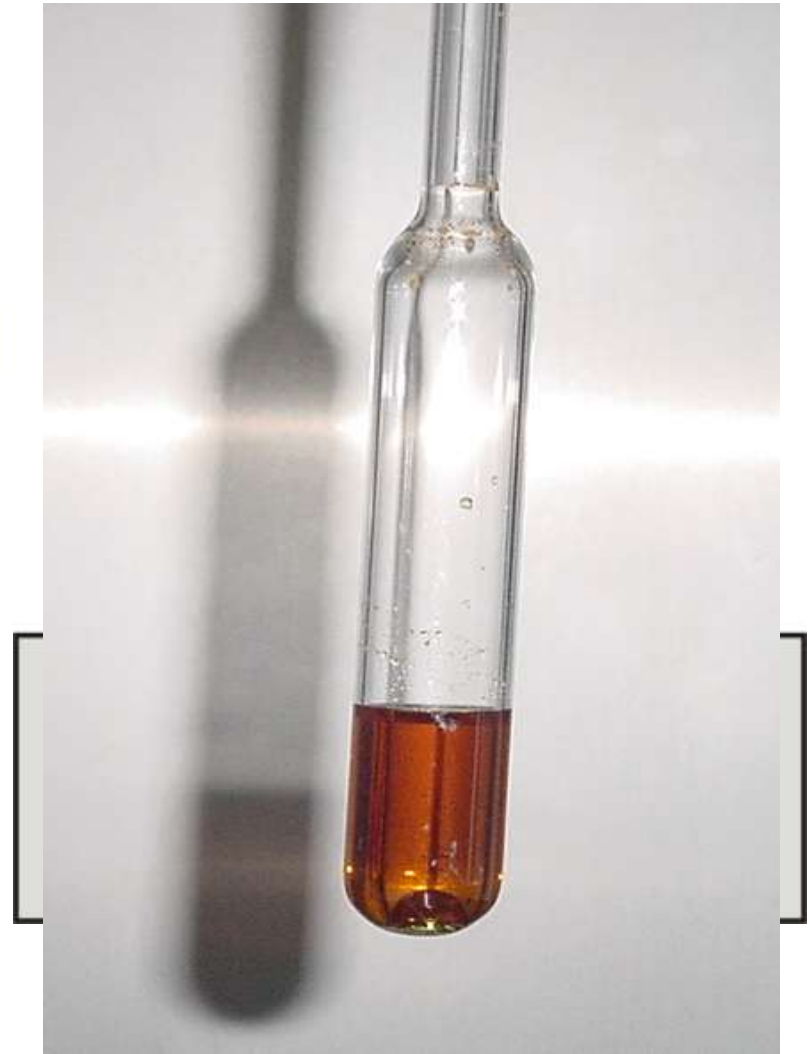
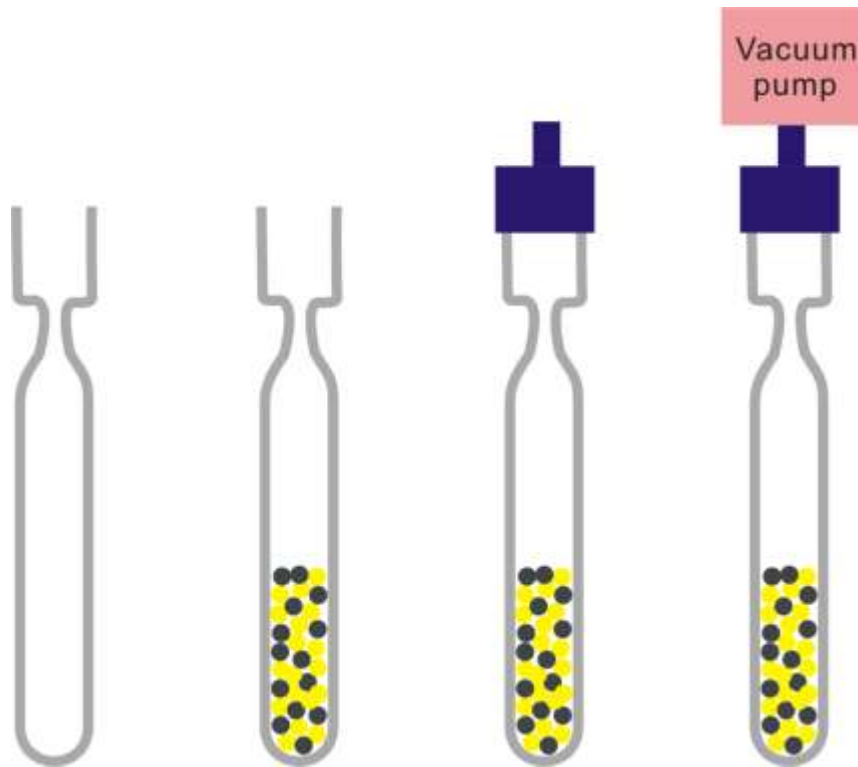
# Glass Melting (Open Atmosphere)



- Wide range of horizontal and vertical tube furnaces, chamber furnaces, high and low temperature ovens, vacuum processing
- Processing in dry nitrogen, argon, oxygen, SF<sub>6</sub>, hydrogen and hydrogen sulphide
- Speciality heating including rapid thermal annealing and RF induction



# Glass Melting – Sealed Ampoule Melting



Typically used for compounding elements, eg. Ge, Se, Te, Sb<sub>8</sub>

## RF Induction Heating

- Clean, precise, controllable heating
- Custom design, interchangeable coils
- Flexible, we configure the furnace to our needs



CIH\_ISM HF20

Up to 20 kW output  
50-150kHz

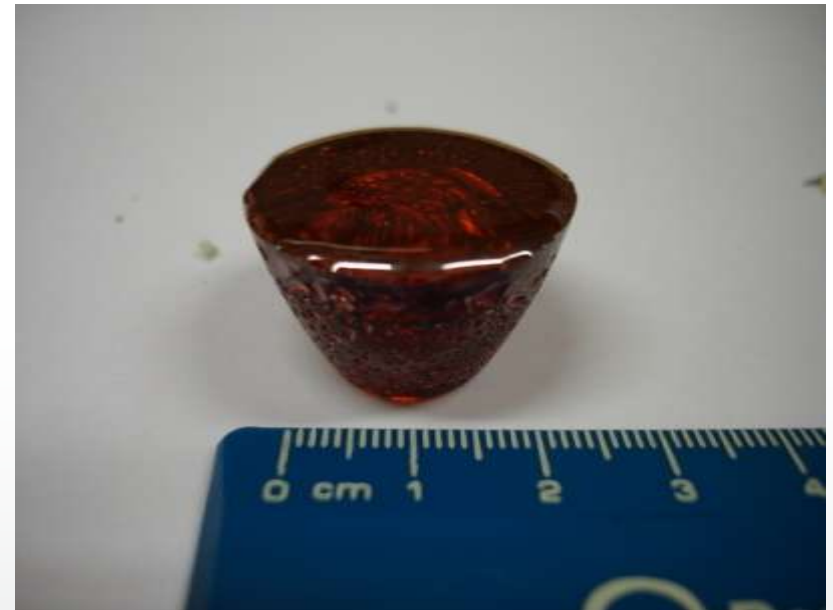


# How Not to Melt Glass



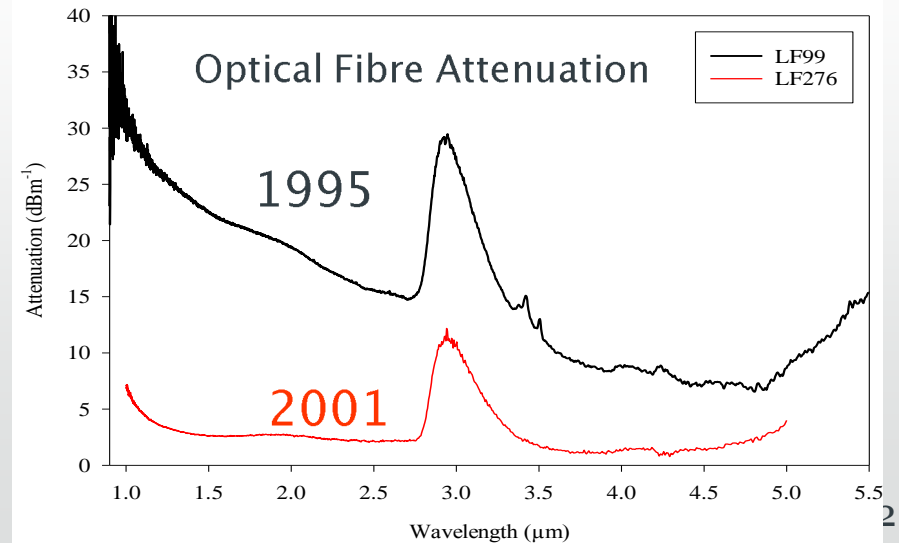
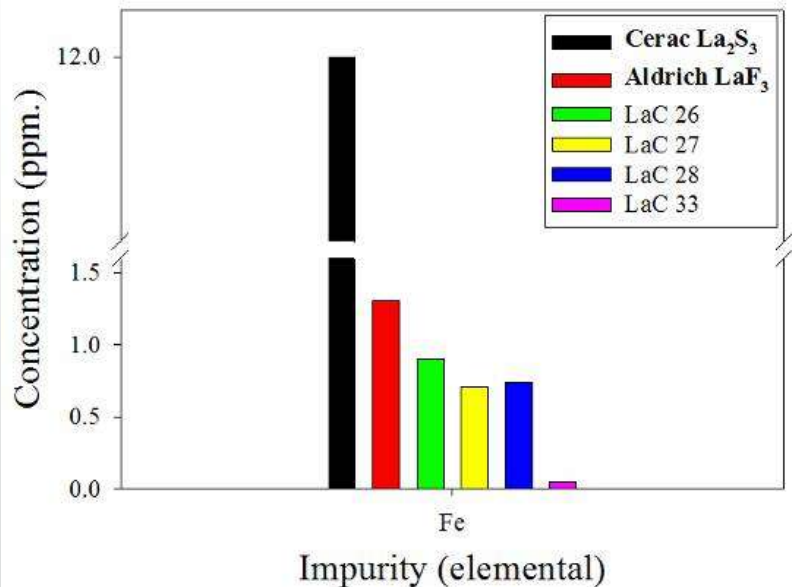
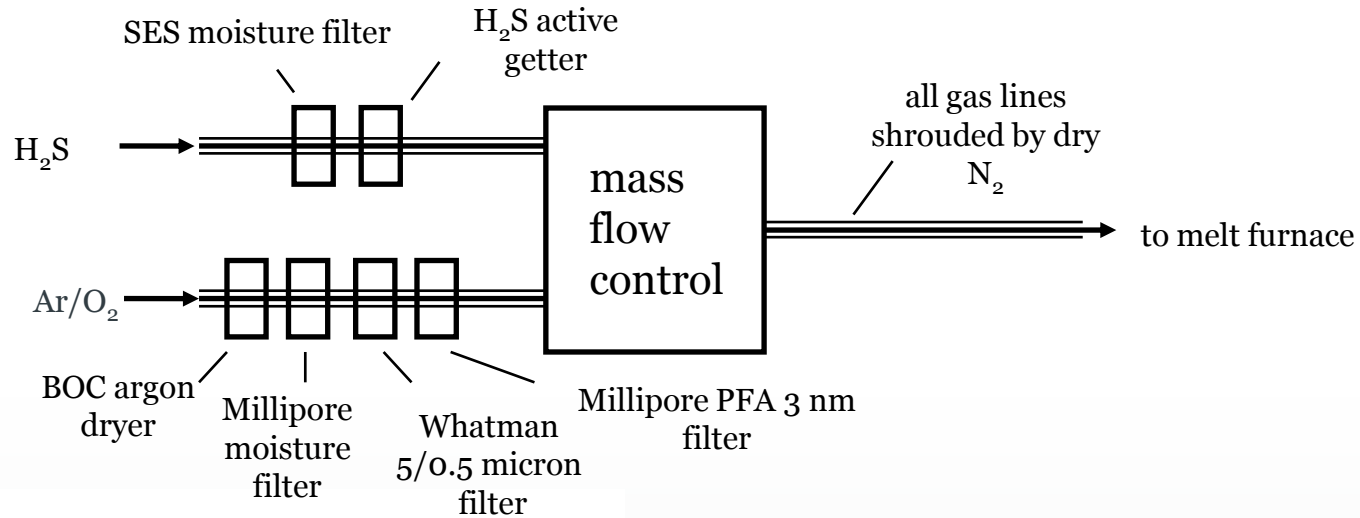
30 October 2005

# Raw Materials are Critical!



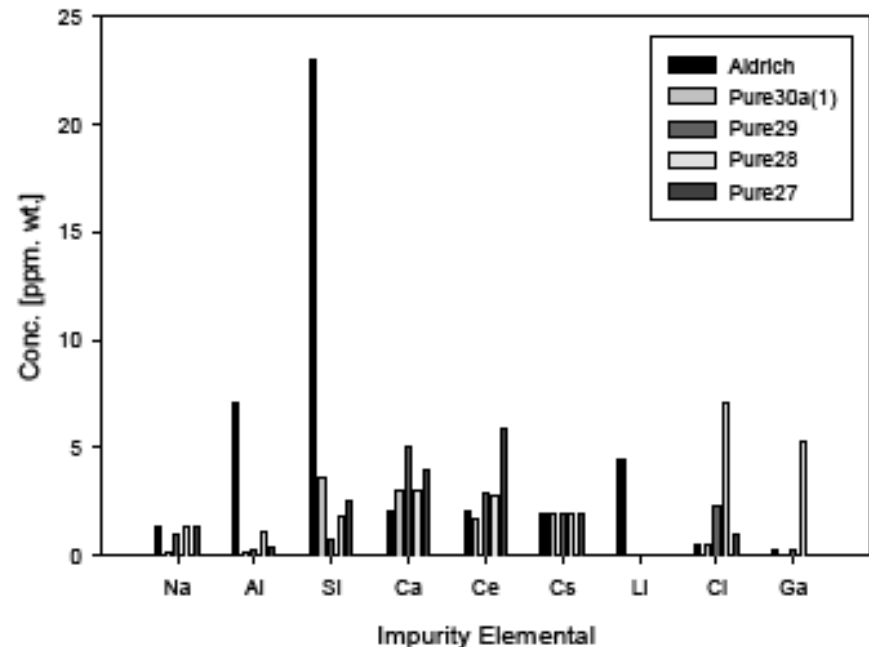
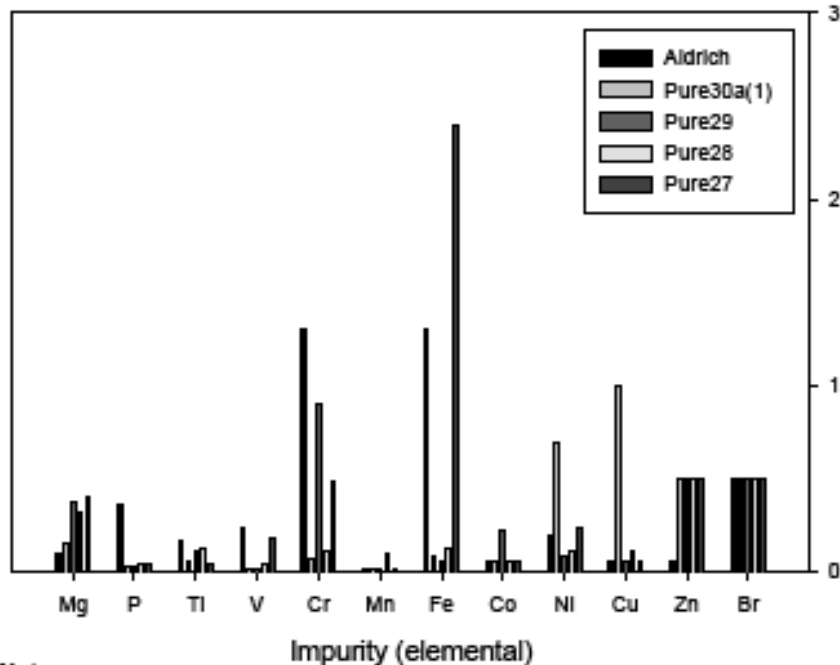
- Ga-La-S-O samples prepared with materials sourced from different manufacturers.
- Melting conditions were identical.

# In-House Designed & Built Gas Delivery



## Purity Levels for LaF<sub>3</sub>

Aldrich vs In-house purified



### Notes

#### Pure30a(1)

Tube + crucibles baked out = 24hrs. Crucible Type = Ceramic x 2  
 Tube clean (though used in Pure 30 / LaCO13 / LaCO14). Powder Mass ~ 6g / 8g

Crucibles exposed to atmosphere for 1min. Slight black colouring on surface after purification.

#### Pure29

Crucible Type = Carbon x 2. Powder Mass ~ 20g / 65g

#### Pure28

Tube + crucibles baked out = 12hrs. New Tube used.  
 Crucible Type = Carbon. Powder Mass ~ 83g  
 Appearance of powder after purification = white

#### Pure27

Tube + crucibles baked out = 12hrs. New Tube used with carbon liner.  
 Crucible Type = Carbon. Powder Mass ~ 60 / 30g

Purification Run	C	O	S
	(Impurity Content in ppm wt)		
Aldrich	140	100	0.71
Pure30a (1)	70	6000	140
Pure29	43	300	-
Pure28	45	570	160
Pure27	65	210	780

# Thermal Properties

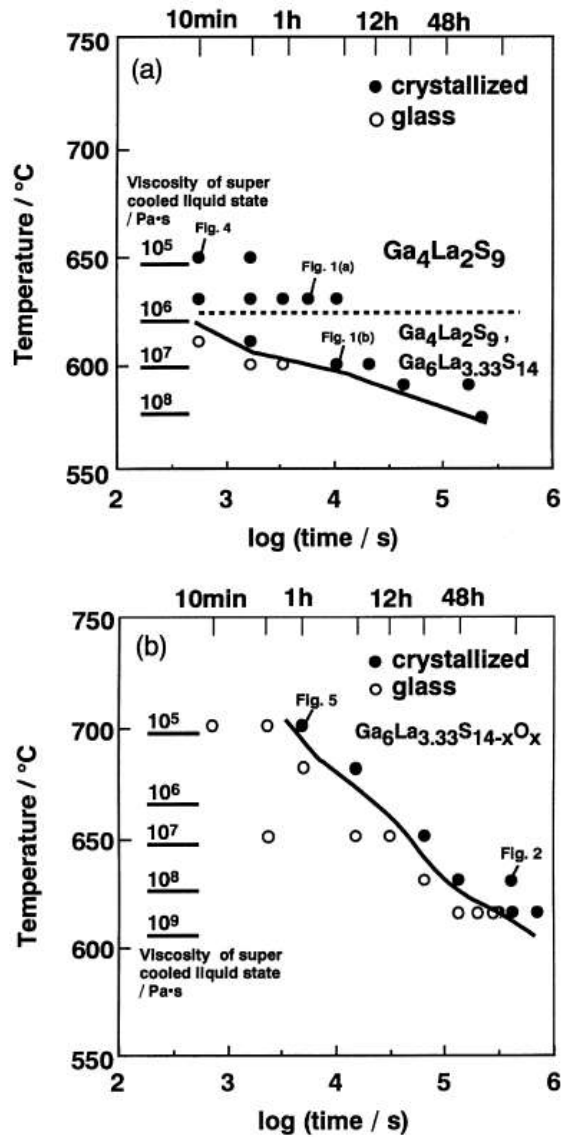


Fig. 3. TTT diagrams of (a) GLS and (b) GLSO glasses during isothermal treatments. Viscosity data of super cooled liquid states is also shown in these figures.

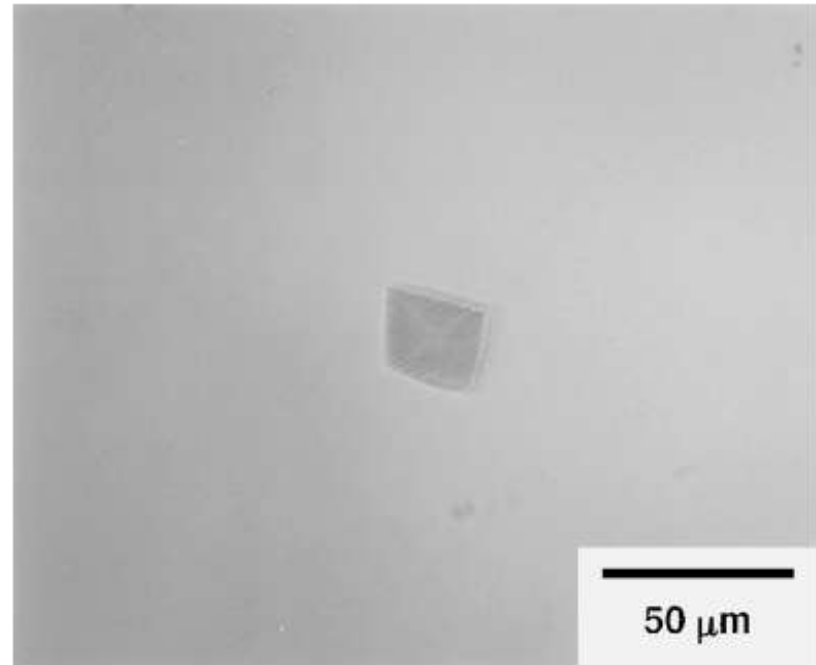








Fig. 5. Transmission optical micrograph of the GLSO glass treated at 700°C for 1 h.

# Glass Modification

○ ORC Research 1992-2005

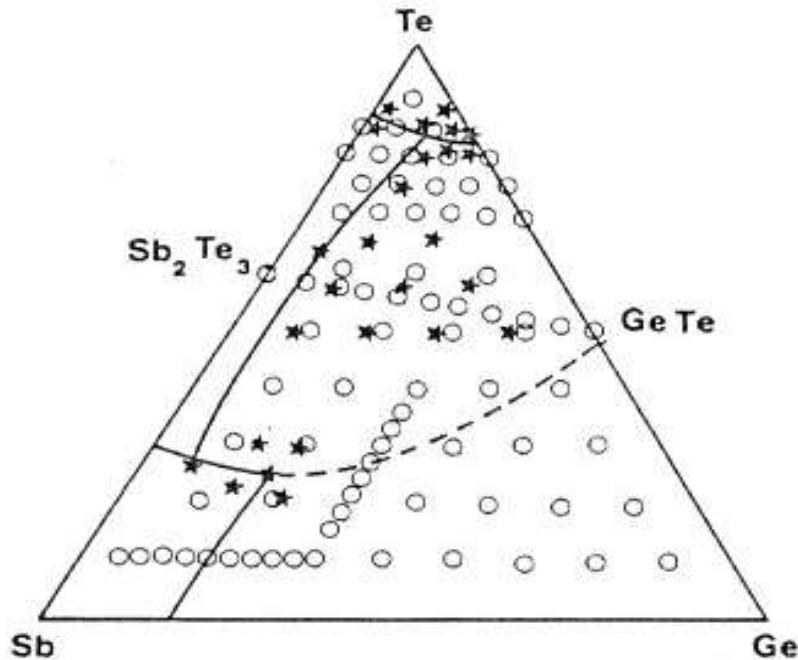
H																	He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	Ac	Rf	Db	Sg	Bh	Hs	Mt									

Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr

-  1<sup>st</sup> Generation  
 US 4115872  
 ~1978
-  2<sup>nd</sup> Generation  
 US 45335219  
 ~1994
-  3<sup>rd</sup> Generation  
 US 5341328  
 ~1994
-  4<sup>th</sup> Generation  
 US 5406509  
 ~1995
-  5<sup>th</sup> Generation  
 US 6011757  
 ~2000
-  Emerging  
 US 4115872  
 ~2003



# Background – Early Mapping of GeSbTe



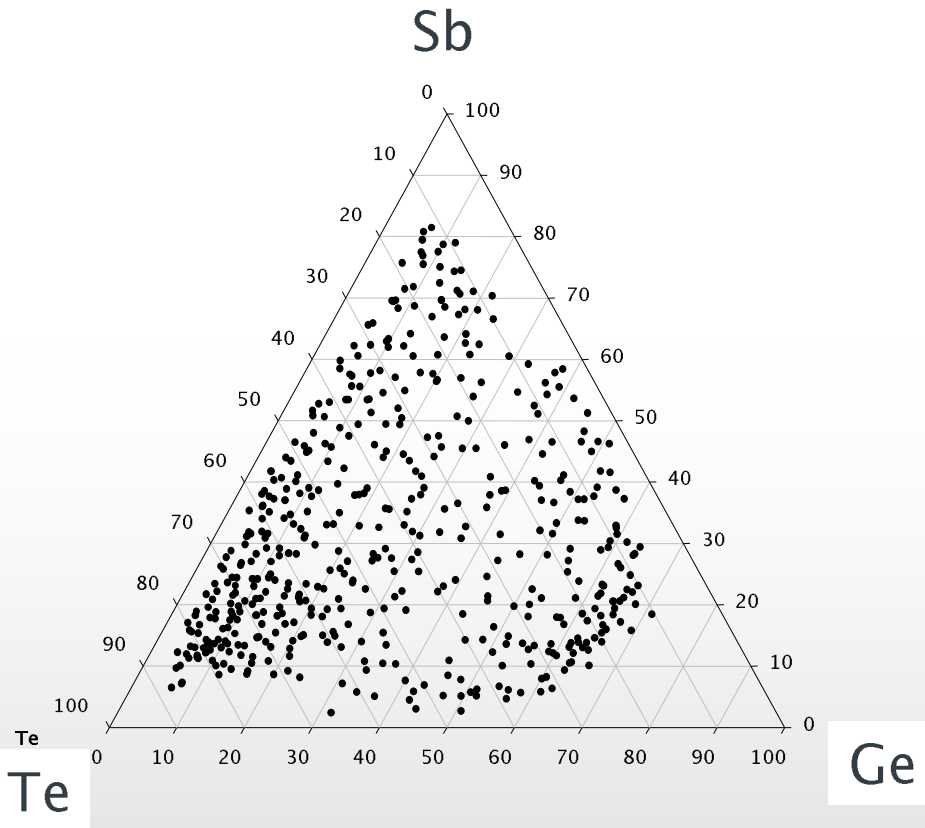
- 100 samples GST alloys studied
- Each melted in sealed ampoules
- Composition individually analyzed
- Melting temperature by DTA
- Tg and crystallization by DSC
- Crystalline phases by XRD

Time Scale: several months?



Science-led Materials Discovery

# Full Ternary Analysis

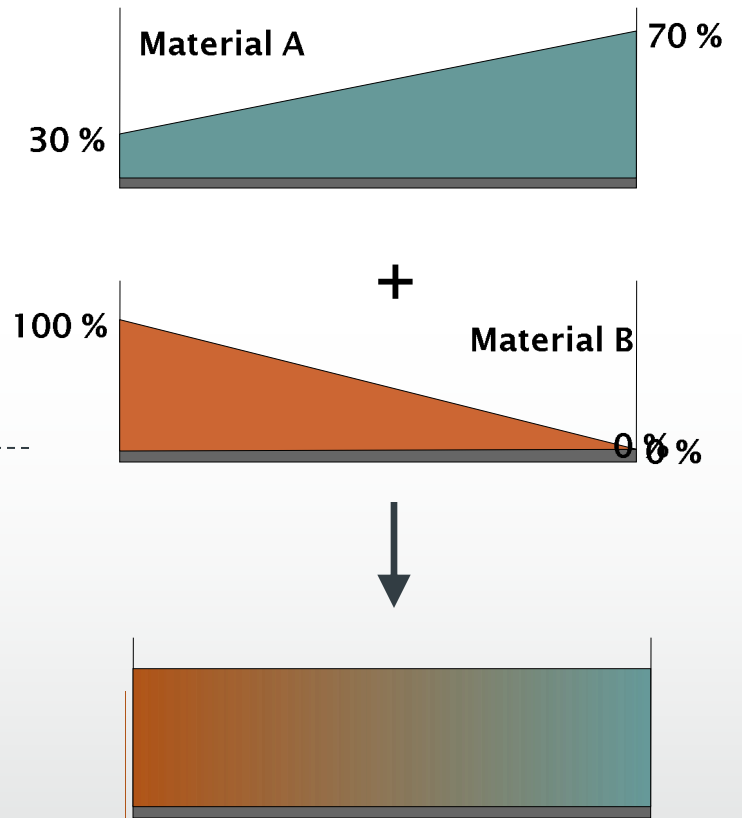
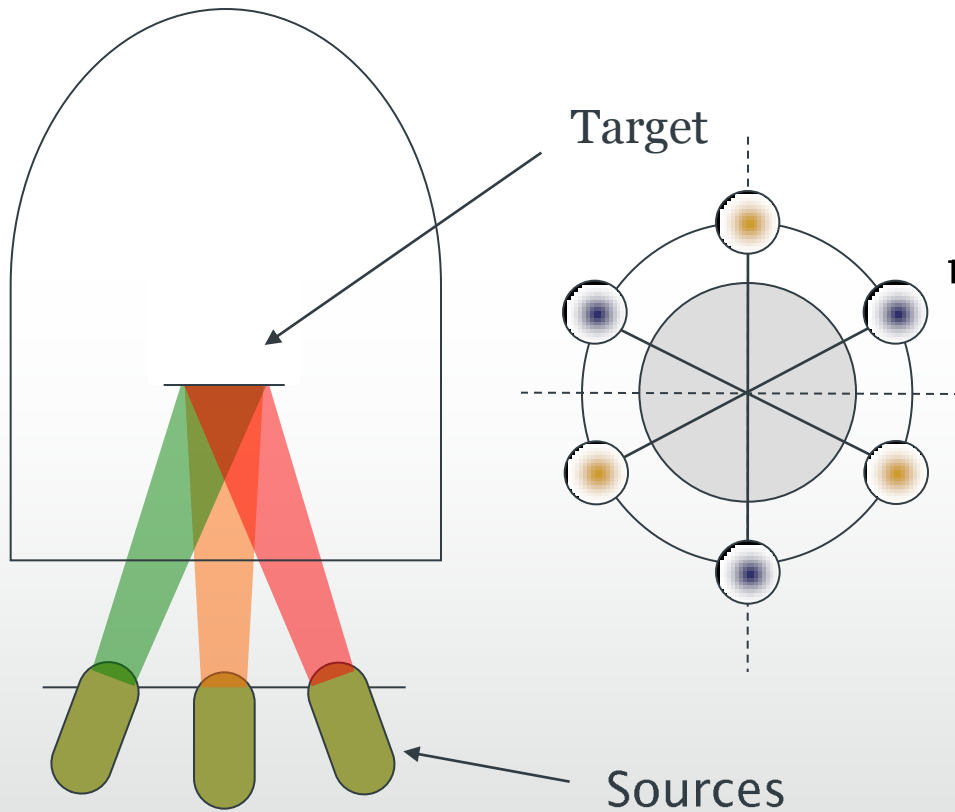


Calibration Runs:	2 - 3 days
Run 653	2 hours
Run 659	2 hours
Run 770	2 hours
Primary Screening	2 - 3 days
Time Scale: one week	

Presented at *EPCOS '05* Cambridge Sep 2005  
R.E.Simpson, D.W.Hewak, S.Guerin, B.Hayden,  
G.Purdy, “High throughput synthesis and screening of  
chalcogenide materials for data storage”

**Pioneering Technology: High Throughput Physical Vapour Deposition**  
Material Discovery Times accelerated by a factor of 10 - 100

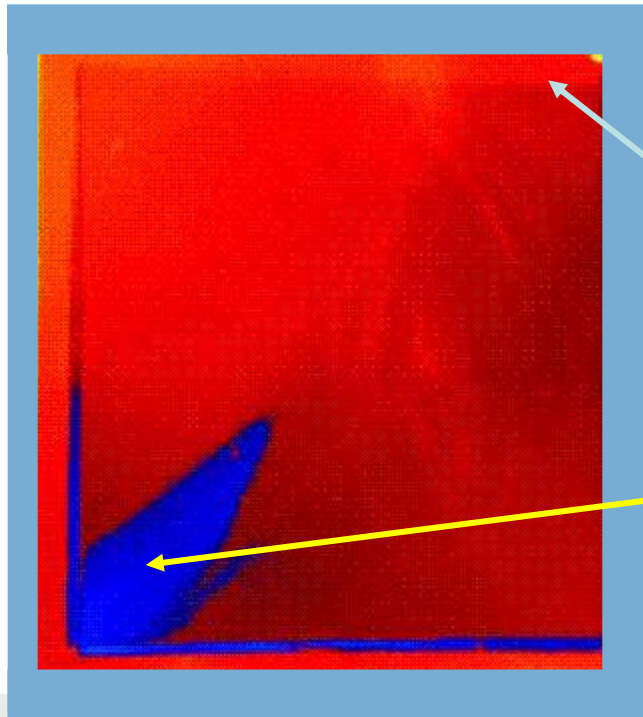
# High Throughput Deposition



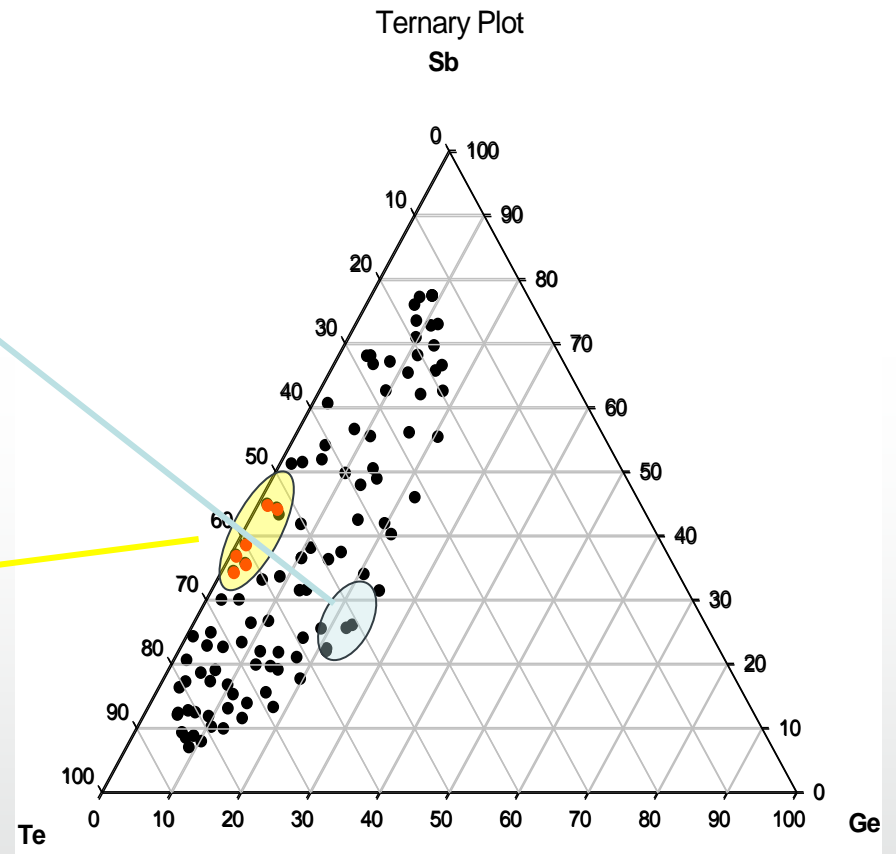
Shutter over each target ensures reproducible and reliable “wedge” which combined gives a desired gradient

# Optical Screening

Hot plate heating

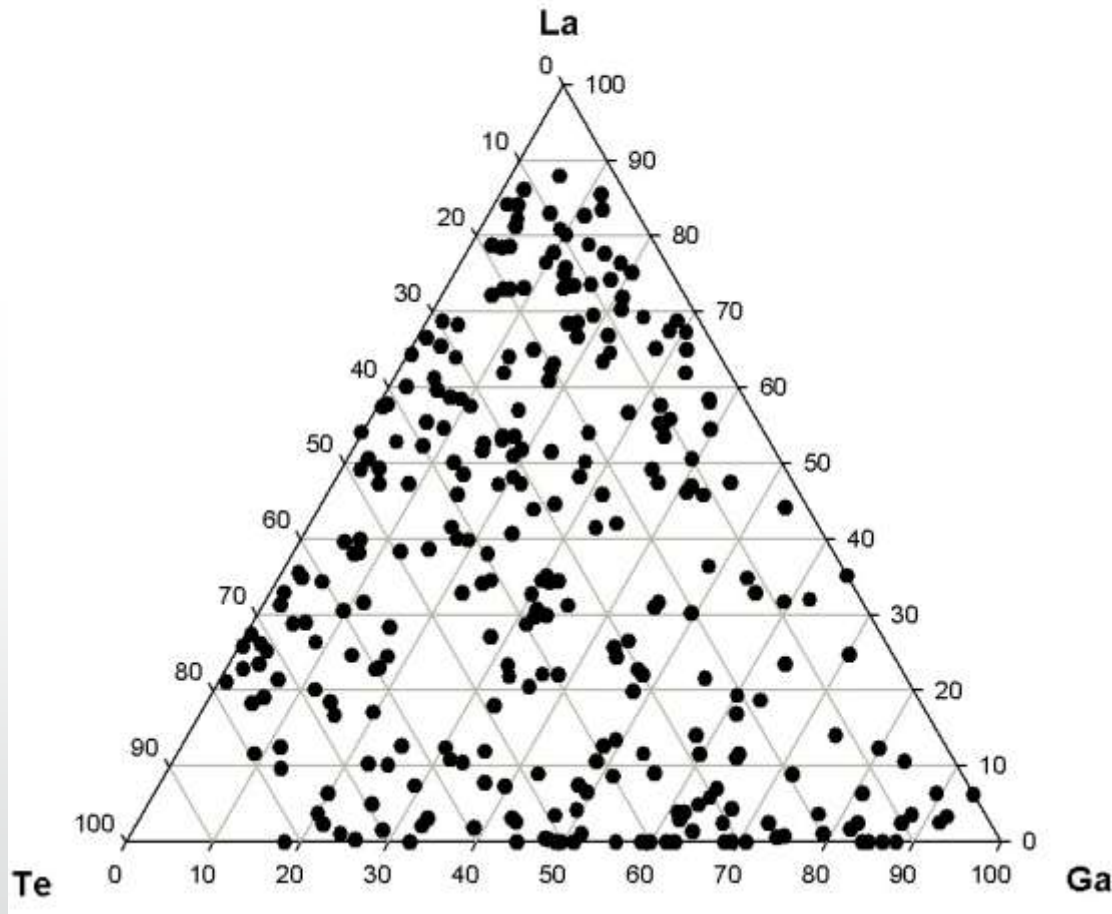


High Sensitivity B&W Progressive Scan  
1392 x 1040 pixel CCD Camera  
Starlight Express Ltd. Model SXV-H9



# Full Compositional Analysis of Ga:Te:La System

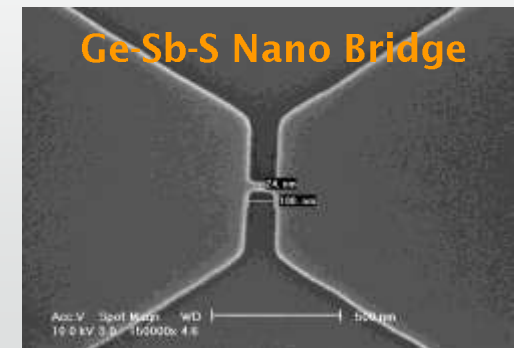
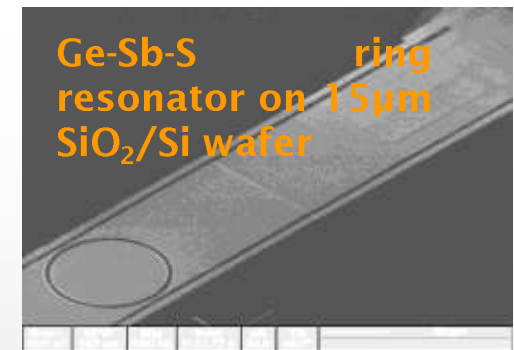
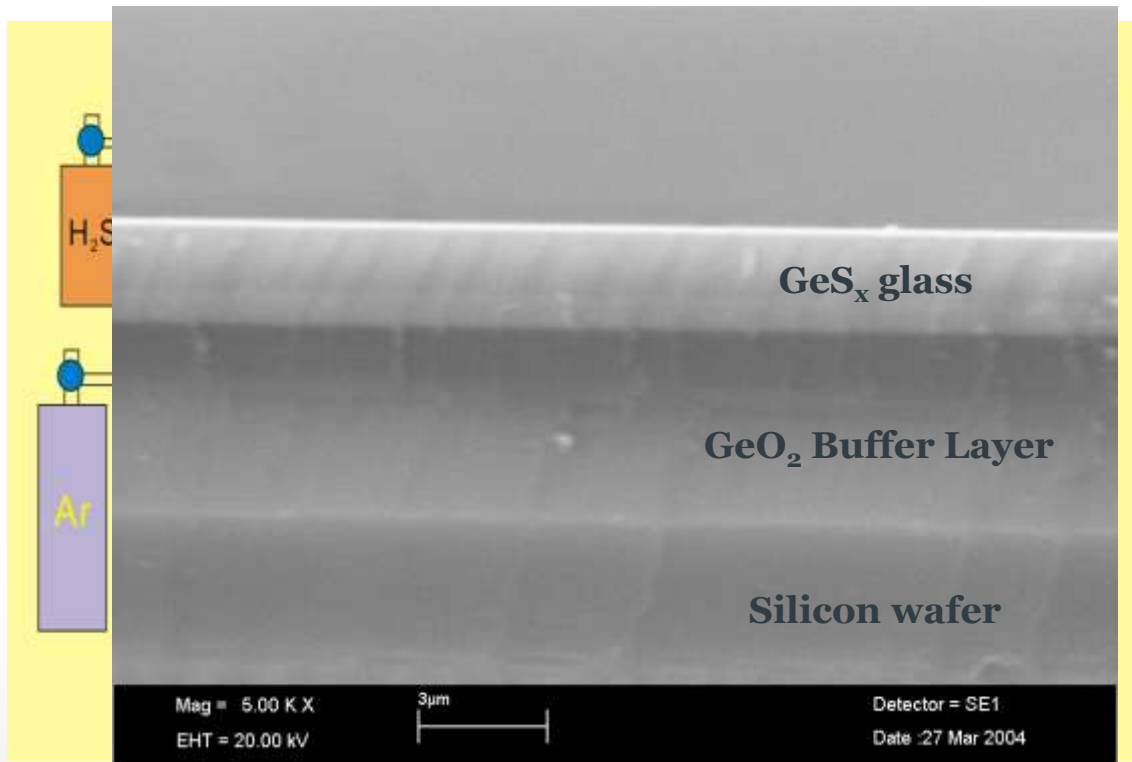
EDS 1613 + 1659



# Optical Fiber



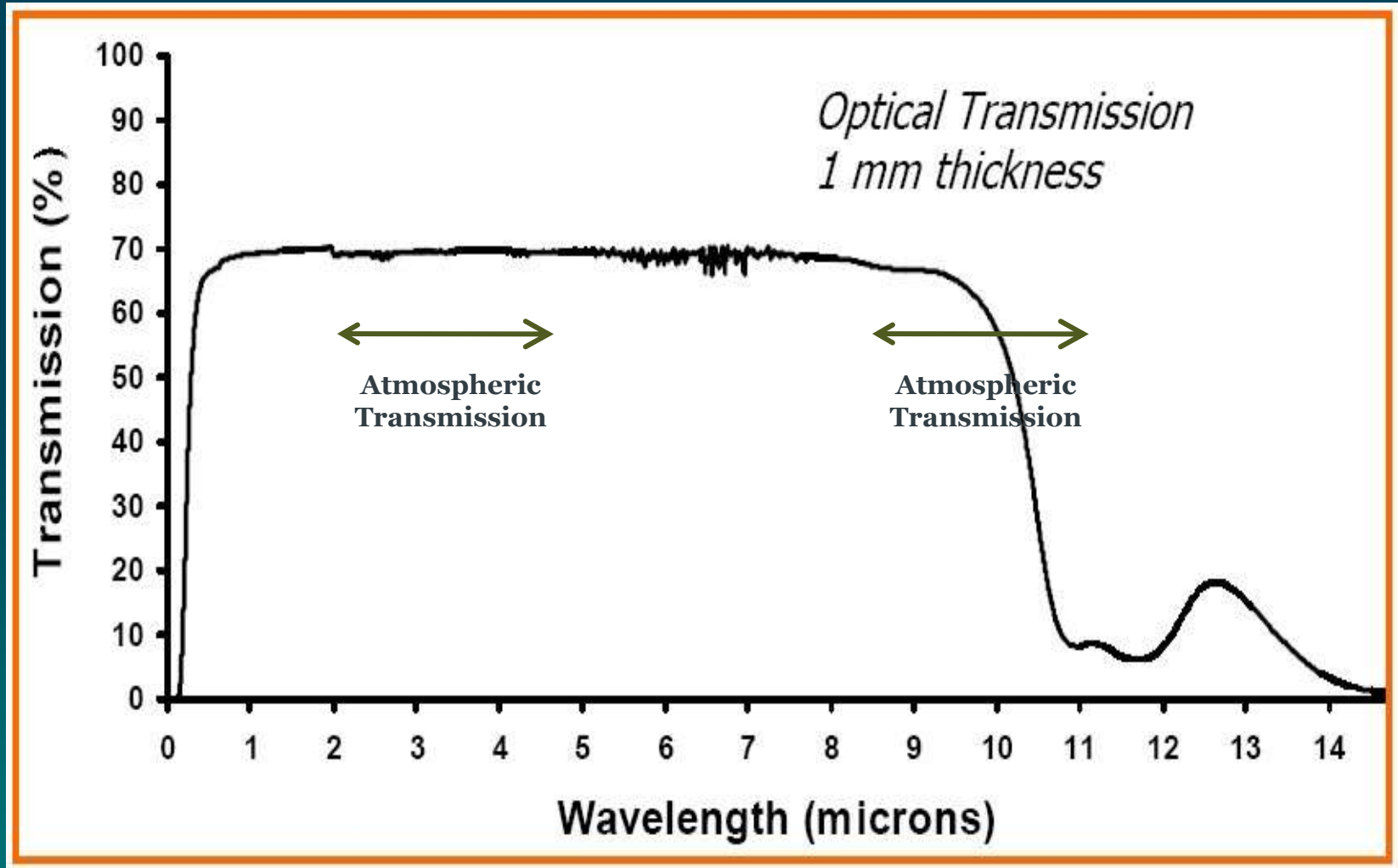
# Chemical Vapour Deposition



**Impurities in glasses prepared by different methods (data in ppm)**

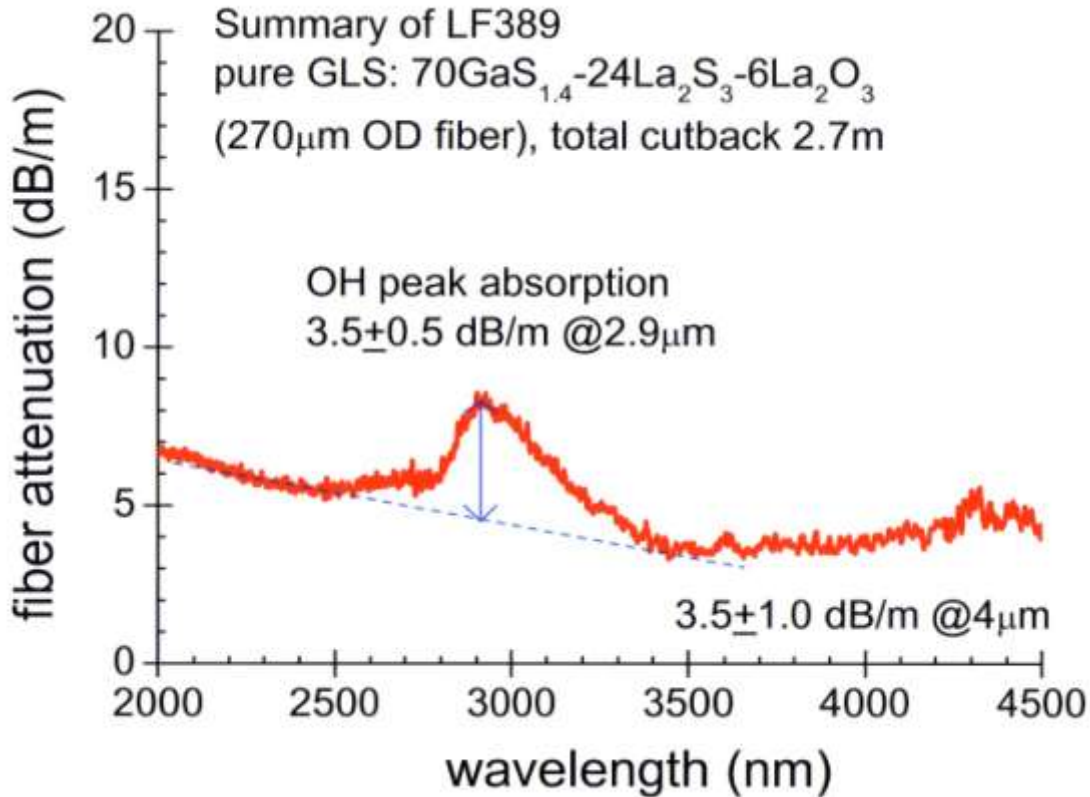
Glass	Preparation Method	Cr	Fe	Co	Ni	Cu	Zn
Ge:S	CVD	<0.005	<0.0 5	<0.0 5	<0.0 5	<0.0 5	<0.05
Ga:La:S	Melt Quench	0.02	0.06	nil	0.04	0.1	<0.5

# Optical Transmission





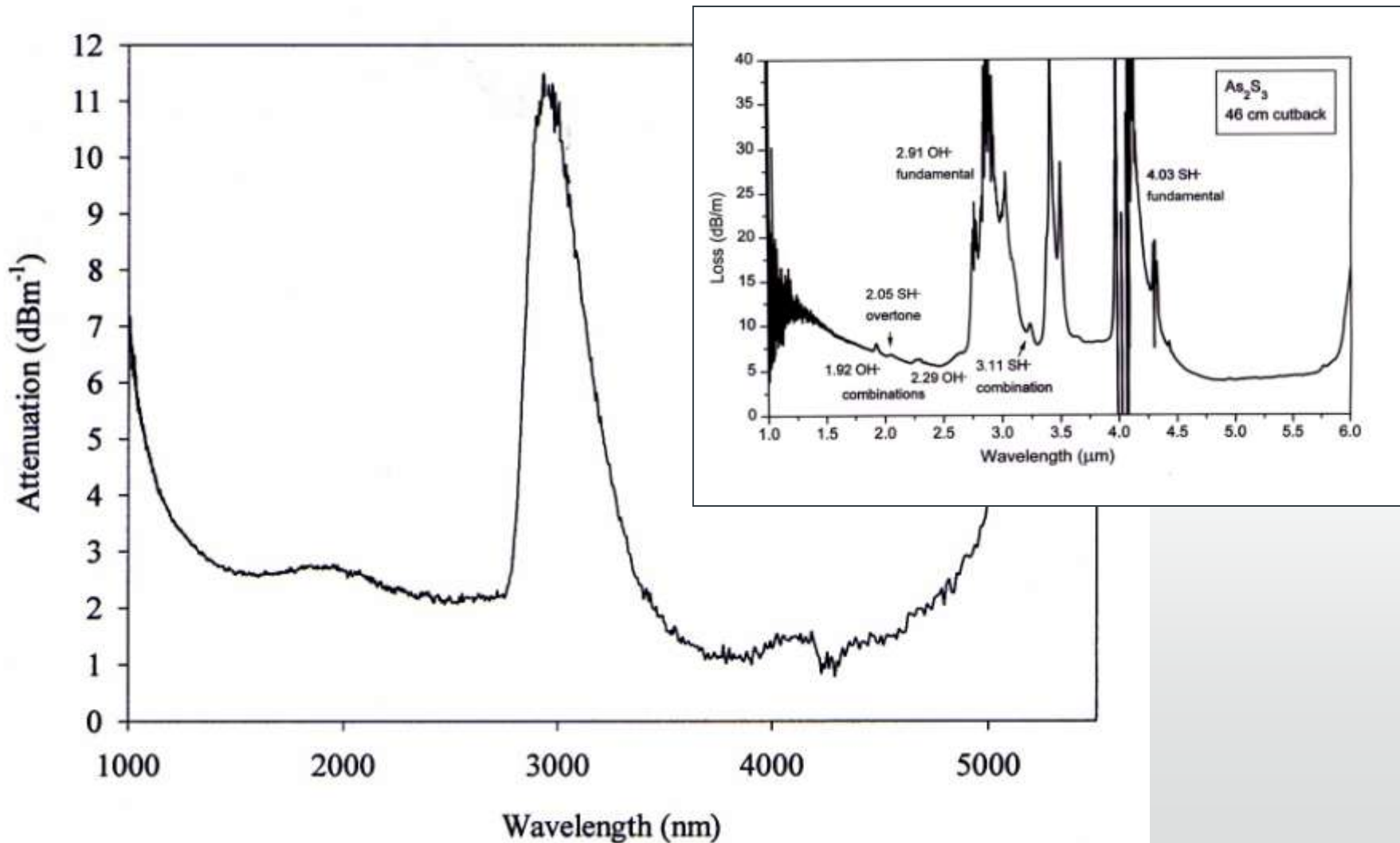
# Optical Fibre Results



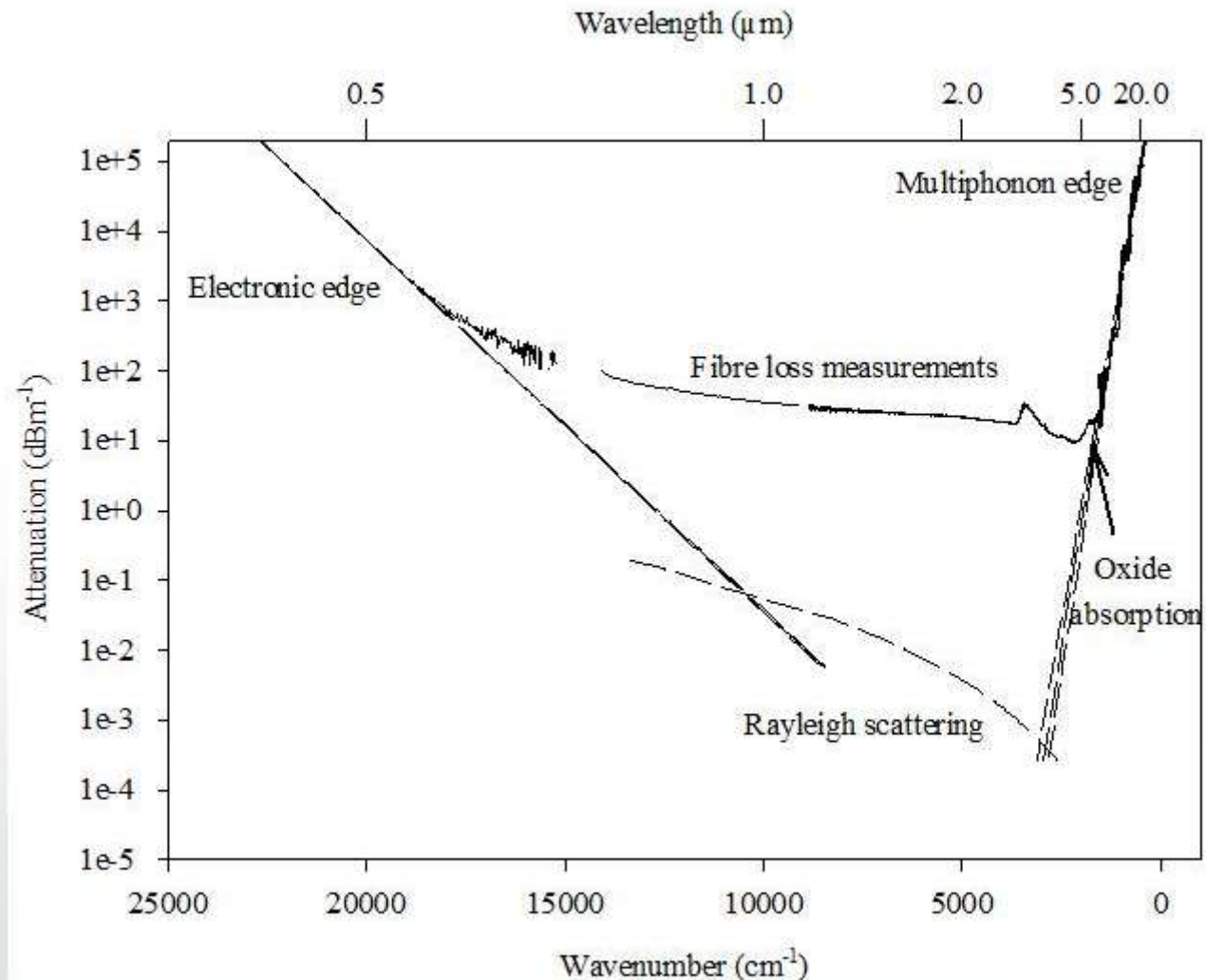
g

	Internal Loss	Optical Fibre
1992	$0.1 \text{ cm}^{-1}$	40 – 60 dB/m
2002	$0.02 \text{ cm}^{-1}$	2-3 dB/m
Target*	0.004	< 0.2 dB/m

# Comparison of GLS fibre with Commercial Arsenic-based fibre



# Theoretical Loss Limits



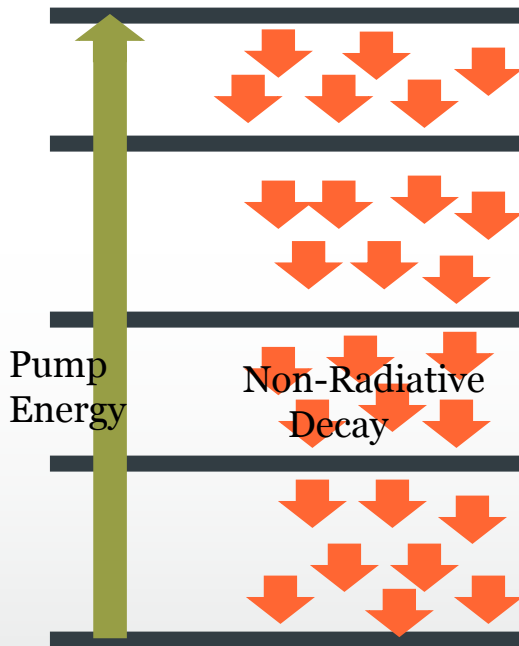
Results in practice are far from predictions!

# Active Devices

- Mid-IR sources
- Microspheres
- Emerging technologies

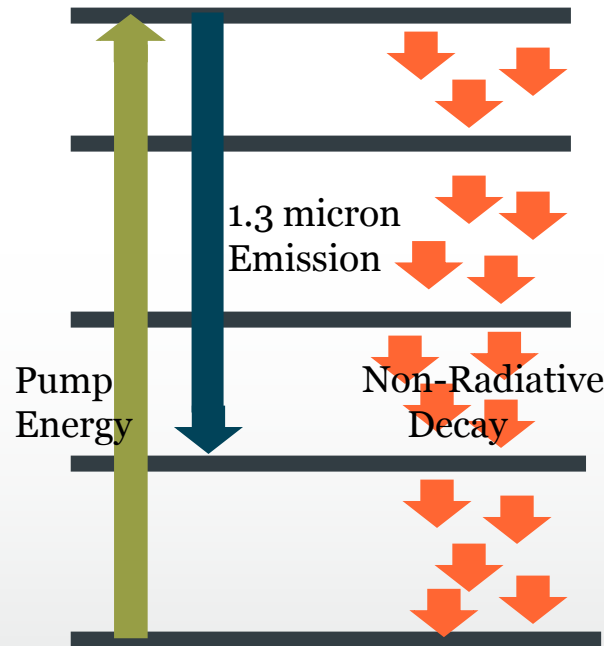
# Glass Structure & Multiphonon Decay

Pr<sup>3+</sup>



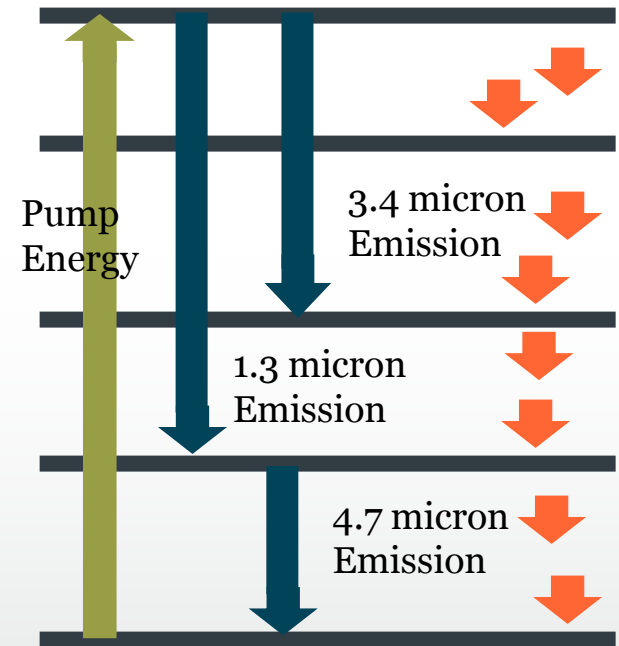
Oxide Glass  
 High Phonon Energy  
 Efficiency = 0%

Pr<sup>3+</sup>



Fluoride Glass  
 Intermediate Phonon Energy  
 Efficiency = 6%

Pr<sup>3+</sup>



Chalcogenide Glass  
 Low Phonon Energy  
 Efficiency = 60%

# Rare Earth Doping

**Rare Earth Elements**

<b>La</b>	<b>Ce</b>	<b>Pr</b>	<b>Nd</b>	Pm	<b>Sm</b>	<b>Eu</b>	<b>Gd</b>	<b>Tb</b>	<b>Dy</b>	<b>Ho</b>	<b>Er</b>	<b>Tm</b>	<b>Yb</b>	<b>Lu</b>
57	58	59	60	61	62	63	64	65	66	67	68	69	70	71

Lanthanides

H																	He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	<b>Y</b>	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	<b>Lu</b>	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	An	Lr														

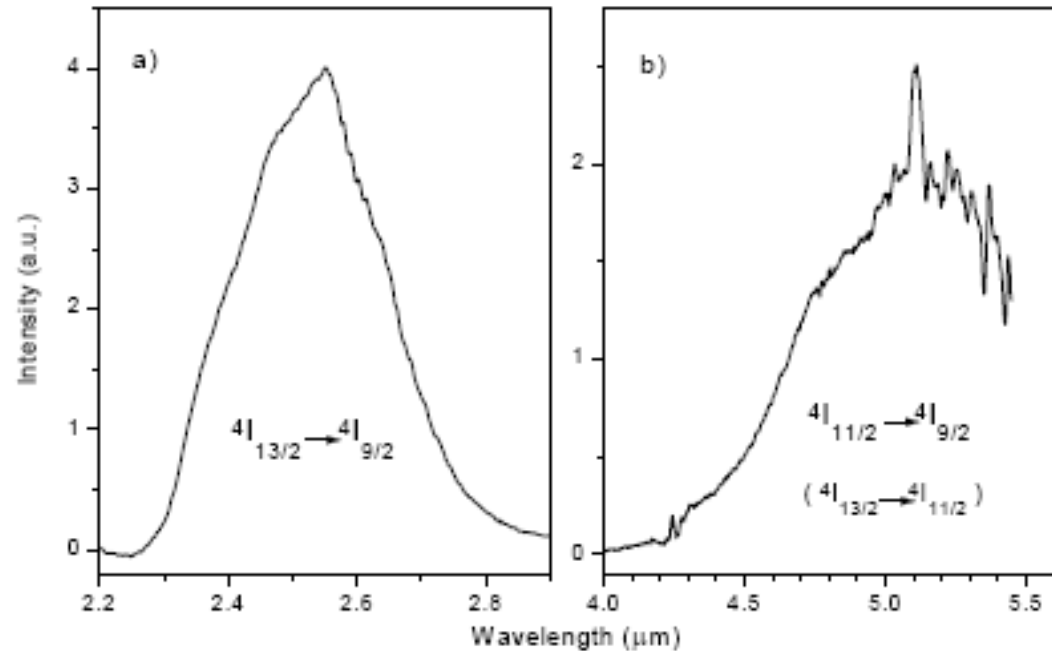


Fig. 6 Emission from the two lowest  $\text{Nd}^{3+}$  levels,  ${}^4\text{I}_{13/2}$  (a) and  ${}^4\text{I}_{11/2}$  (b), in 1.5 mol%  $\text{Nd}_2\text{S}_3$  doped GLS glass pumped at 815 nm with a Ti:sapphire laser and with a 300-mm monochromator and a liquid nitrogen cooled InSb measured detector

$\text{Nd}^{3+}$

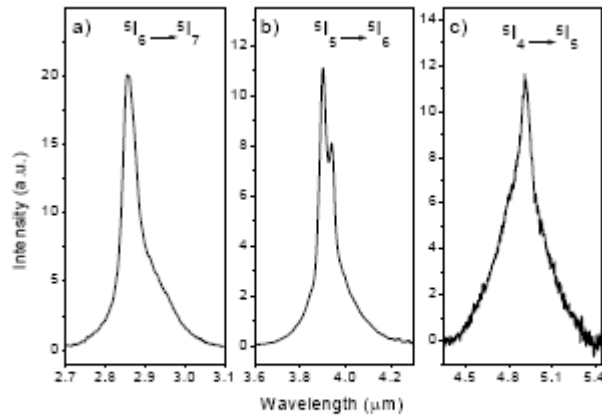


Fig. 5 Mid-infrared emission a) from the  $^5I_6$  level, b) from the  $^5I_5$  level, and c) from the  $^5I_4$  level in Ho(1.5%):GLS pumped at 0.76  $\mu\text{m}$

**Ho<sup>3+</sup>**

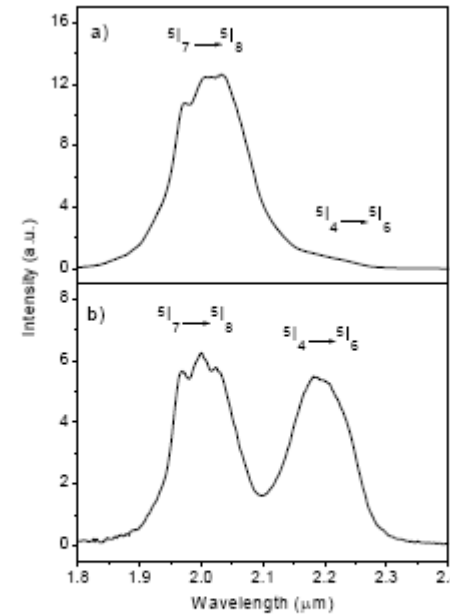


Fig. 3 Overlapping emission at 2.0 and 2.2  $\mu\text{m}$  from the  $^5I_7$  and the  $^5I_4$  levels in Ho(1.5%):GLS pumped at 0.76  $\mu\text{m}$   
 a) continuous wave pump laser  
 b) pump laser chopped at 400 Hz



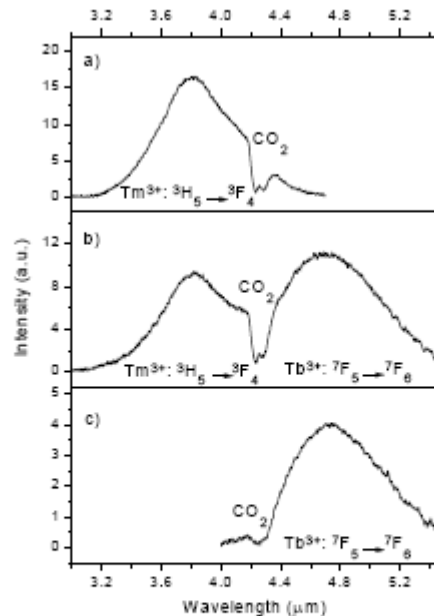


Fig. 7 Uncorrected fluorescence spectra of  
 a) Tm(1.5%):GLS glass pumped at 0.7  $\mu\text{m}$   
 b) Tm(1.5%),Tb(0.2%):GLS glass pumped at 0.7  $\mu\text{m}$   
 c) Tm(1.5%),Tb(0.2%):GLS glass pumped at 2  $\mu\text{m}$

# Tm<sup>3+</sup> and Er<sup>3+</sup>

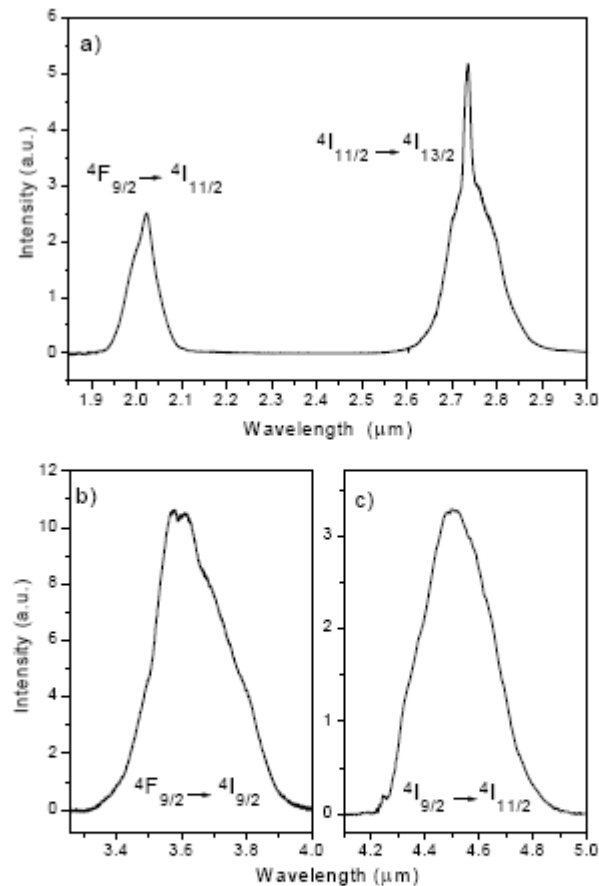


Fig. 4 Fluorescence spectra of 1.57 mol% Er<sup>3+</sup> doped GLS glasses and fibres  
 a) 2.0  $\mu\text{m}$  and 2.75  $\mu\text{m}$  emission from 3.9 cm of 270  $\mu\text{m}$  diameter fibre pumped with 60 mW at 660 nm  
 b) 3.6  $\mu\text{m}$  emission from 8.6 cm of 270  $\mu\text{m}$  diameter fibre pumped with 70 mW at 660 nm  
 c) 4.5  $\mu\text{m}$  emission from a bulk glass sample pumped with 570 mW at 810 nm

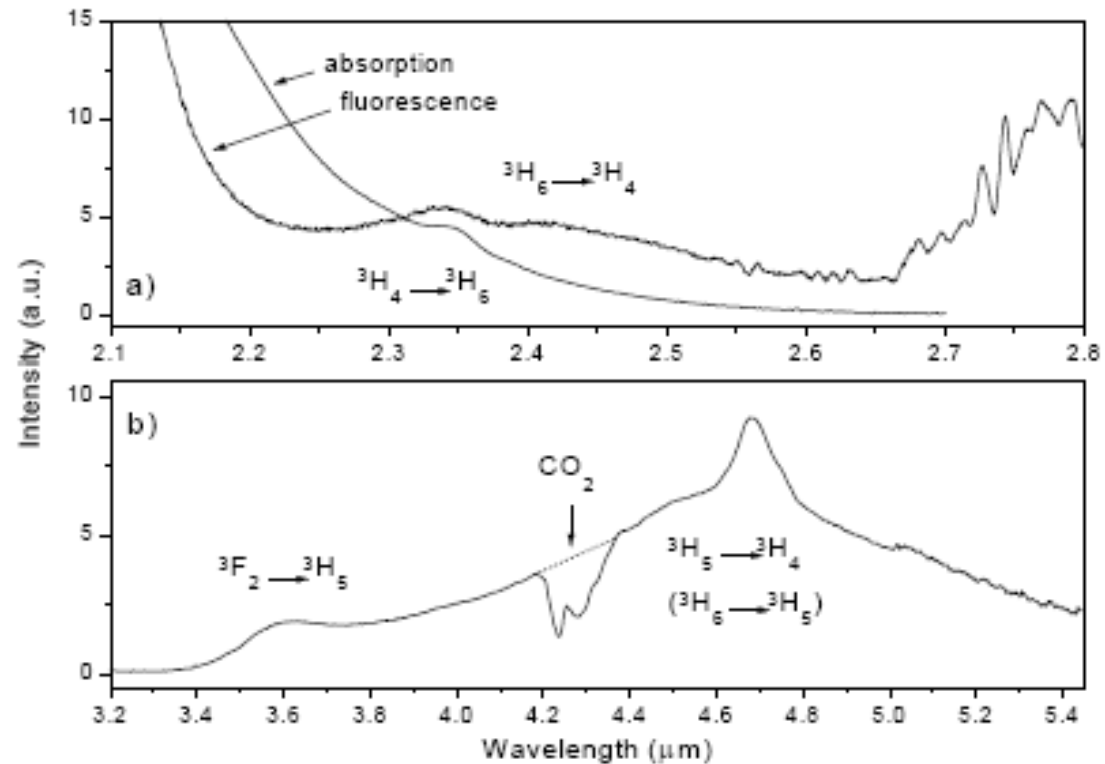
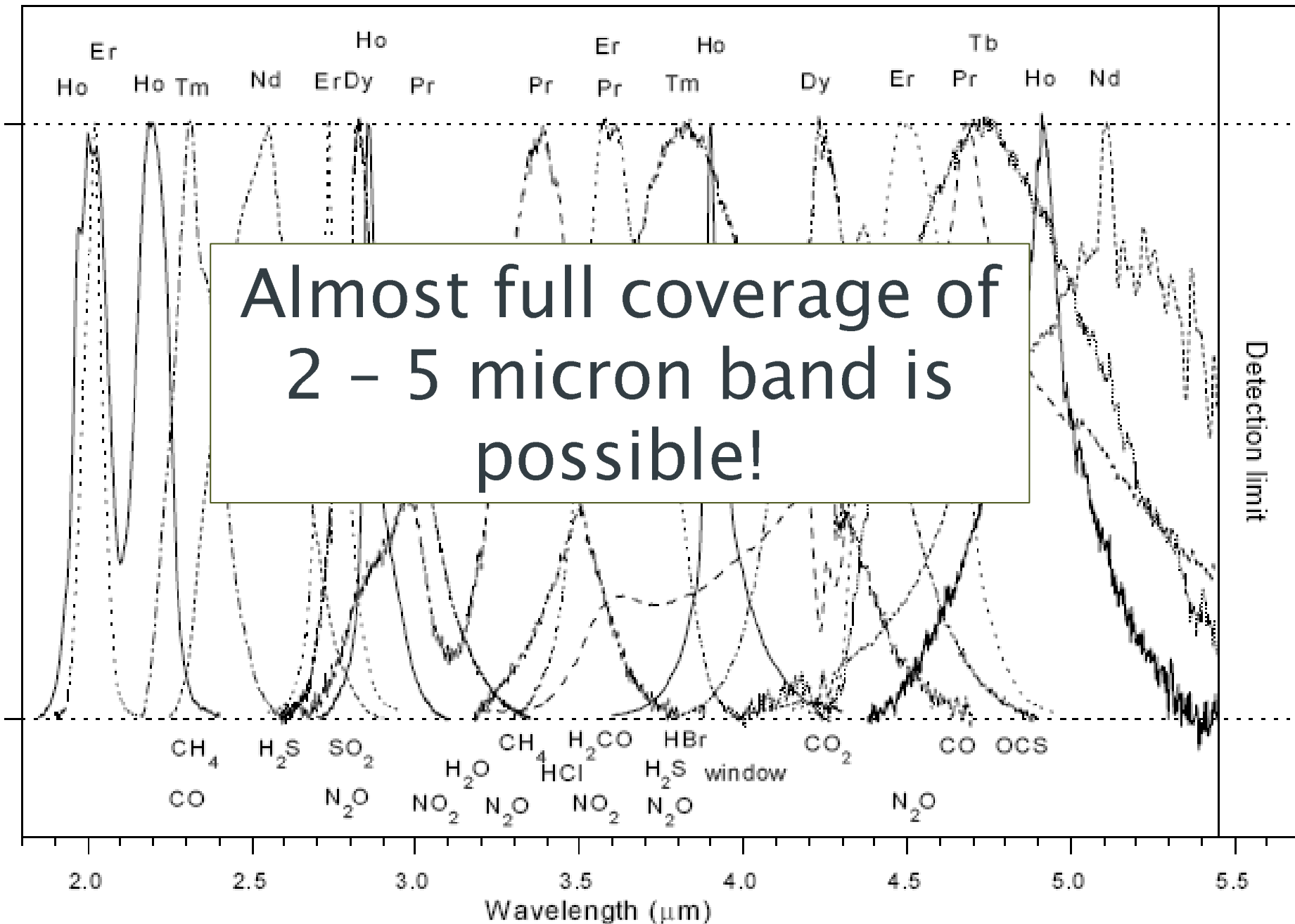


Fig. 3.4.4 Emission from three lower Pr<sup>3+</sup> levels:  
 a) Fluorescence from 2 m long, 500 ppm Pr<sup>3+</sup> doped GLS fibre pumped with 1.064 μm Nd:YAG laser and absorption spectrum  
 b) Fluorescence from 2000 ppm Pr<sup>3+</sup> doped GLS bulk glass pumped with 2 μm Tm:YAG laser

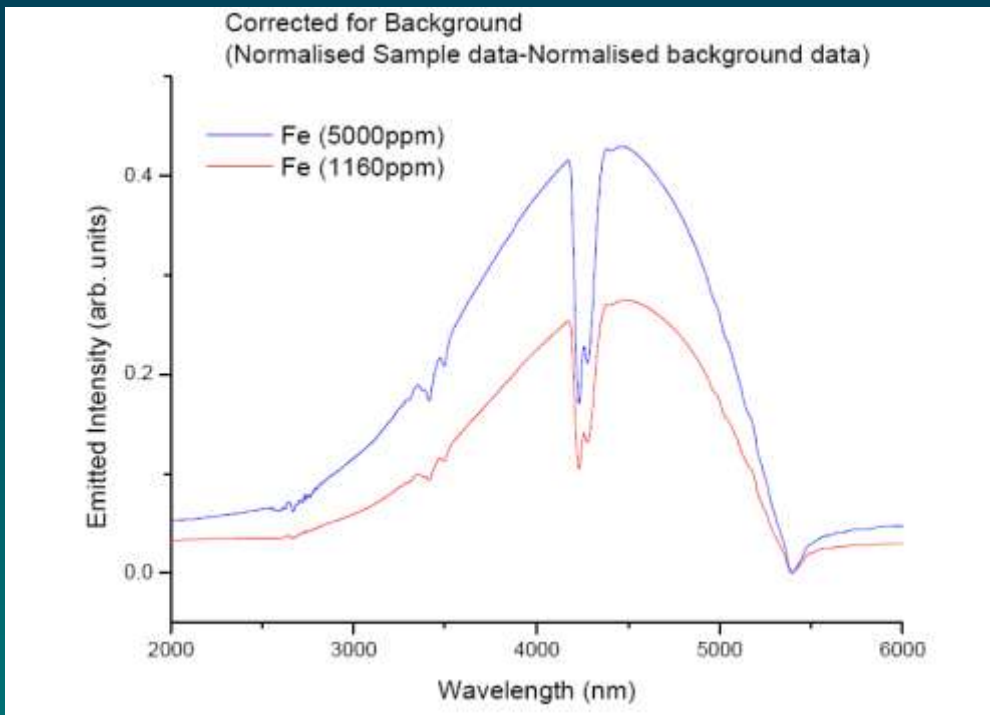
Pr<sup>3+</sup>

Normalised intensity



# Transition Metal Doping

IIIB	IVB	VB	VIB	VIBB	VII			IB	IB
21	22	23	24	25	26	27	28	29	30
Sc	Ti	Y	Cr	Mn	Fe	Co	Ni	Cu	Zn



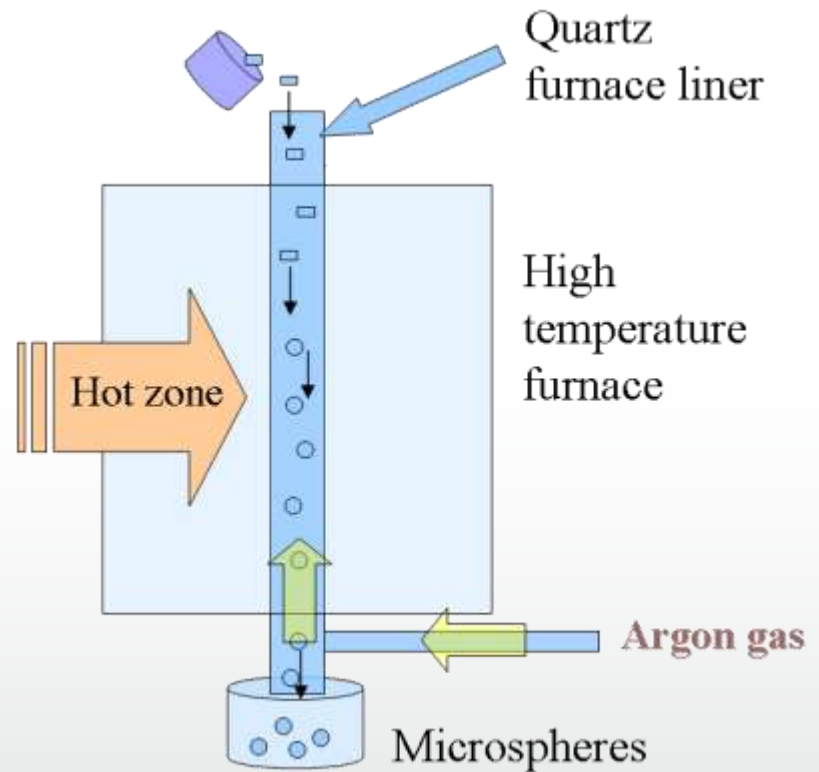
Direct Emission Mid-IR Lasers

Research Contract from UK Laser Coalition  
DSTL, Qinetiq, BAe Systems, Selex

# Microspheres



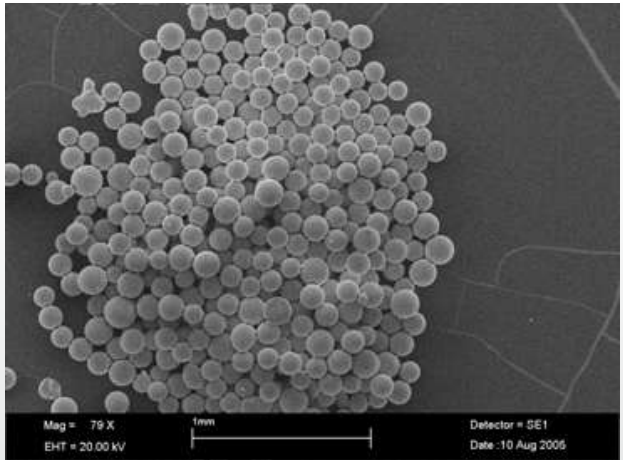
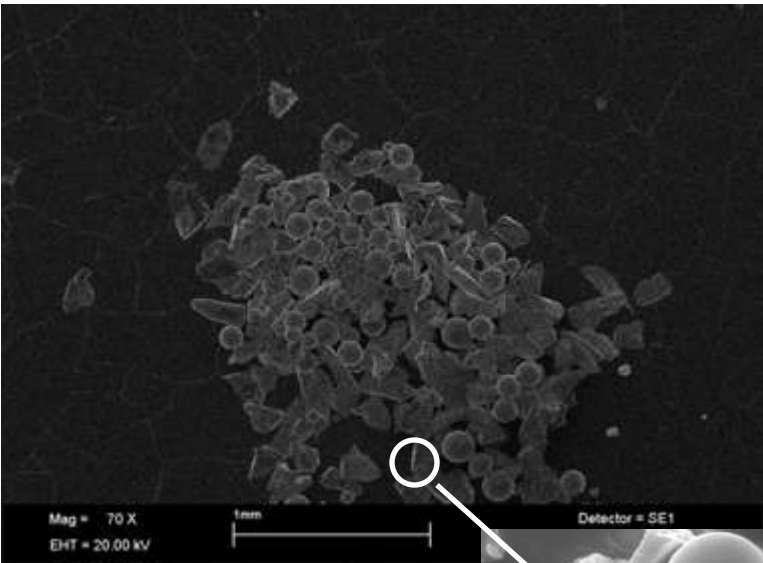
# Microsphere Fabrication



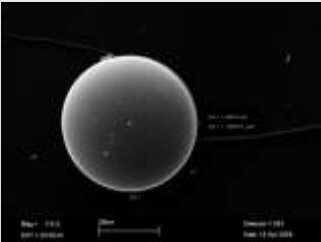
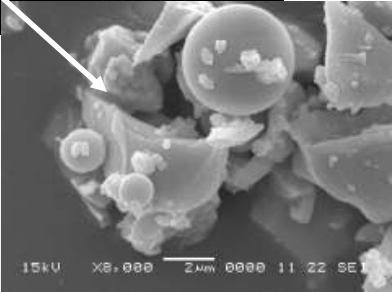
Microsphere diameters 500 nm to 500  $\mu\text{m}$

# Sphere Sorting

sieving  
sedimentation  
rolling



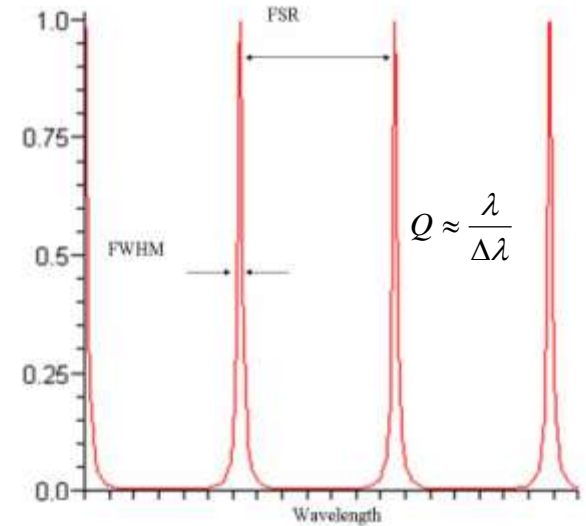
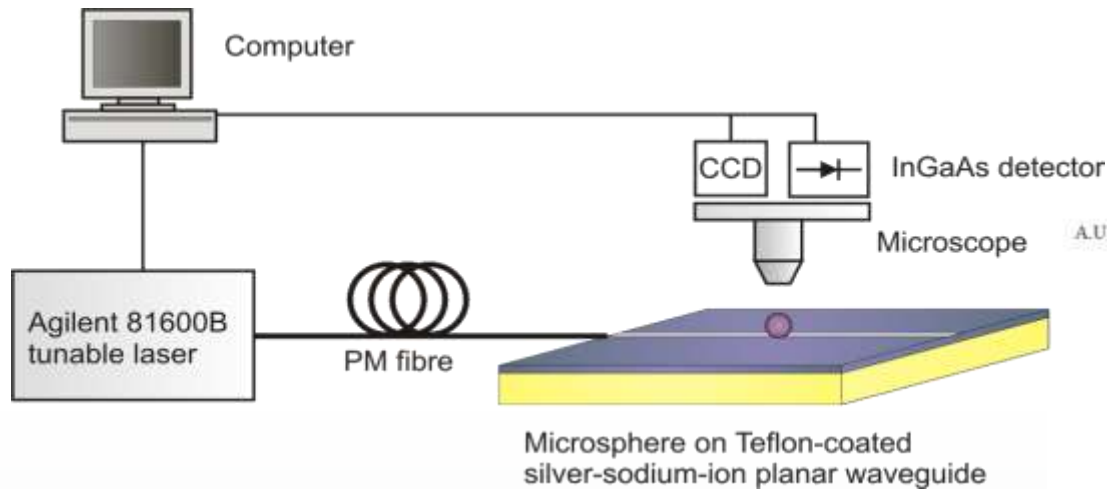
as fabricated...



Size range:  
100's nm to 100's microns

Greg Elliott

# Microsphere Characterization

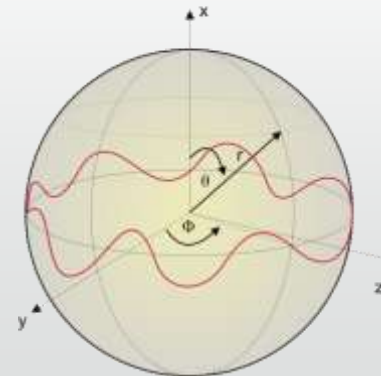


Quality Factor:  $Q$  where  $1/Q = 1/Q_{\text{material}} + 1/Q_{\text{surface}} + 1/Q_{\text{curvature}} + 1/Q_{\text{coupling}}$

$$Q_{\text{predicted}} = \sim 4 \times 10^9$$

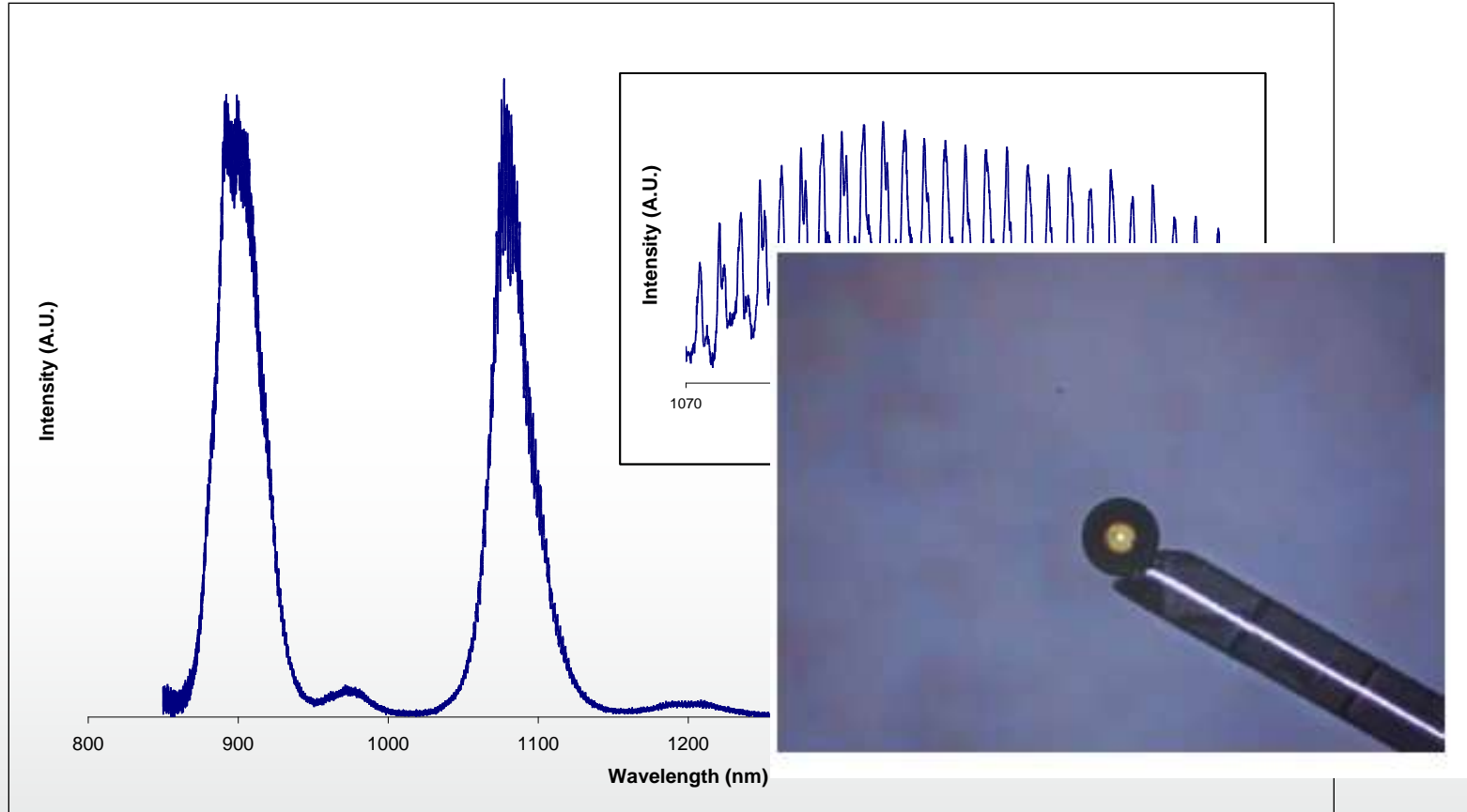
$$Q_{\text{measured}} = 8 \times 10^4$$

Gregor R. Elliott, Daniel W. Hewak, G. S. Murugan, and James S. Wilkinson, "Chalcogenide glass microspheres; their production, characterization and potential", Optics Express, Vol. 15, Issue 26, pp. 17542-17553



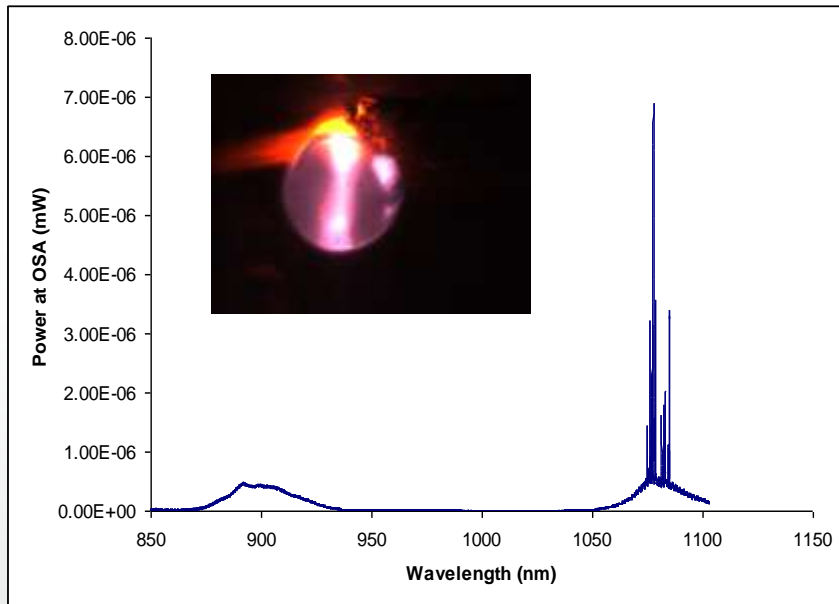


# Improved Coupling

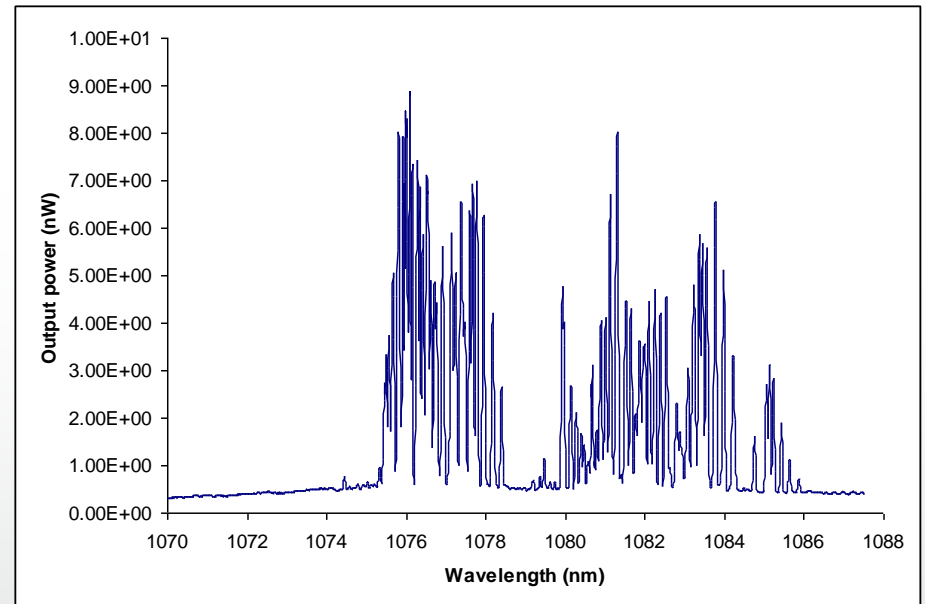


**Fluorescent spectrum from GLS microsphere doped with 1.5mol% Nd. Inset, close up on WGM. This measurement was taken using a fibre coupled microsphere.**

# Initial Lasing Observations



217 mW Pump Power



Maximum Pump Power

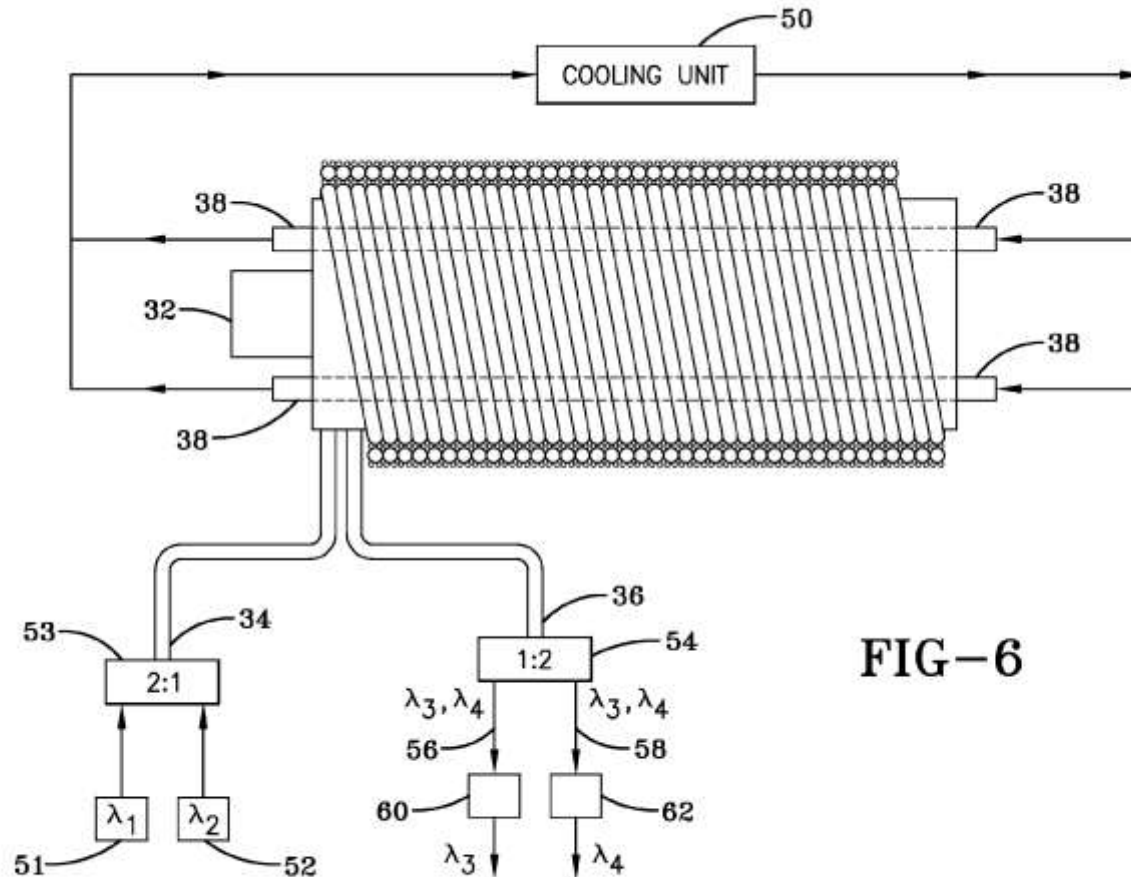
Laser Threshold: 82 mW delivered to sphere

(19) **United States**

(12) **Patent Application Publication**  
ABDELDAYEM

(10) **Pub. No.:** US 2008/0212620 A1

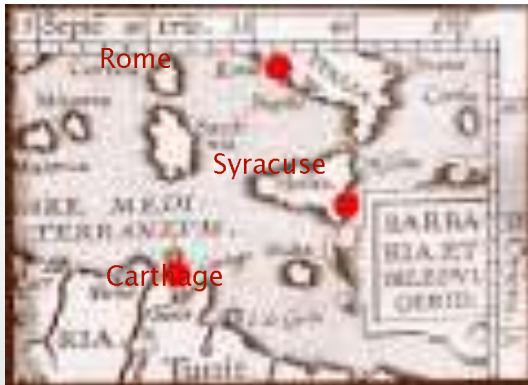
(43) **Pub. Date:** Sep. 4, 2008



**FIG-6**

# UV-Vis-NIR Spatial Beam Combination

## First ever defence application ...



Siege of Syracuse  
2<sup>nd</sup> Punic War - 214 BC



Burning Mirrors of Archimedes

# Characteristics of Microsphere Lasers

- Extremely low threshold
- Simple, robust cavity, easily fabricated
- Integratable with planar or fibre technology
- Potential for new wavelengths in IR

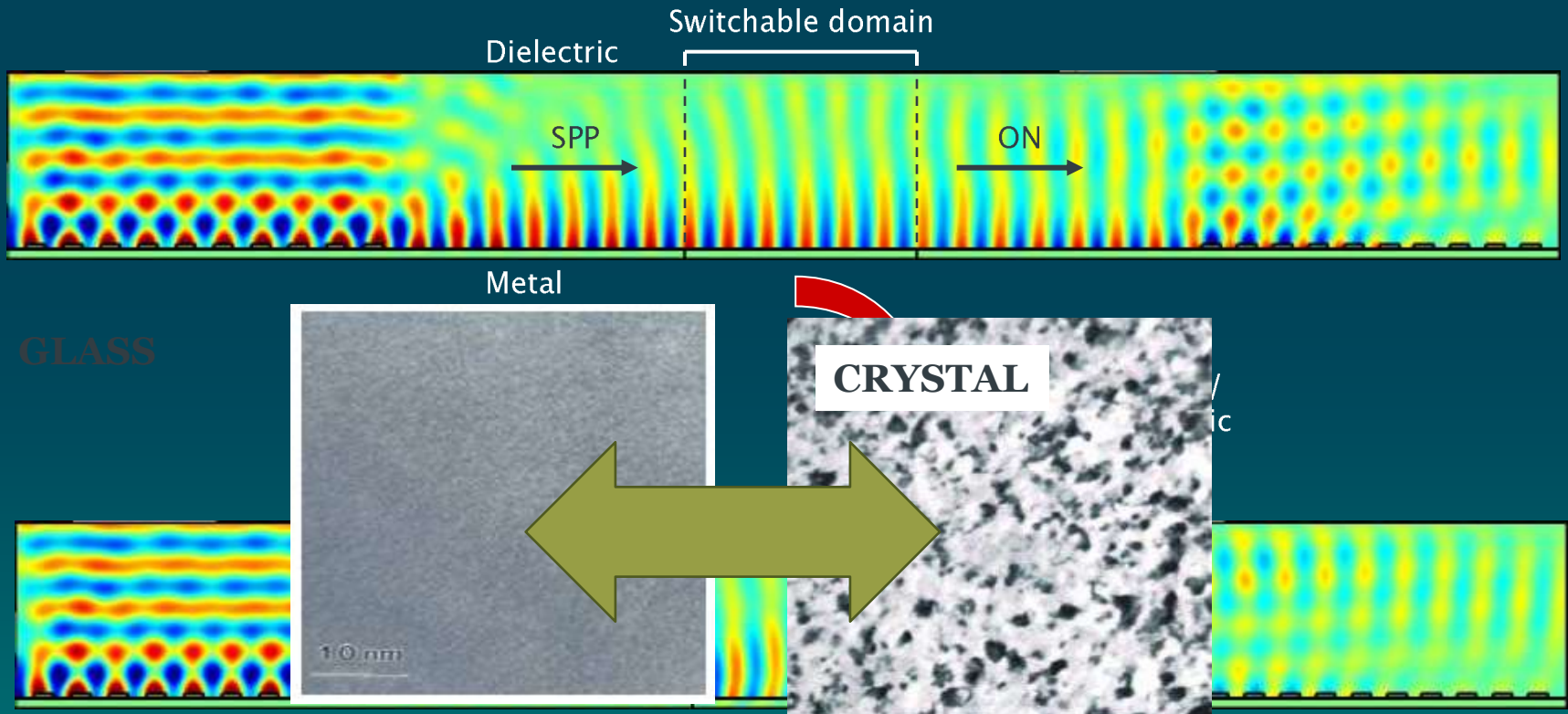
# Application of Phase Change in Nanophotonics



- Plasmonics
- Metamaterials

<http://www.nanophotonics.org.uk/>

# Active Plasmonics ... The Concept



- Transient changes in waveguide properties control SPP propagation.
- Short-range atomic transitions
  - Low free electron density
  - High activation energy
  - High resistivity
  - Transparent
  - High free electron density
  - Low activation energy
  - Low resistivity
  - Opaque
- APL 84, 1416 (2004)

# Ga-La-S Plasmonics

Ge-Sb-Te (GST) unsuitable for plasmonics

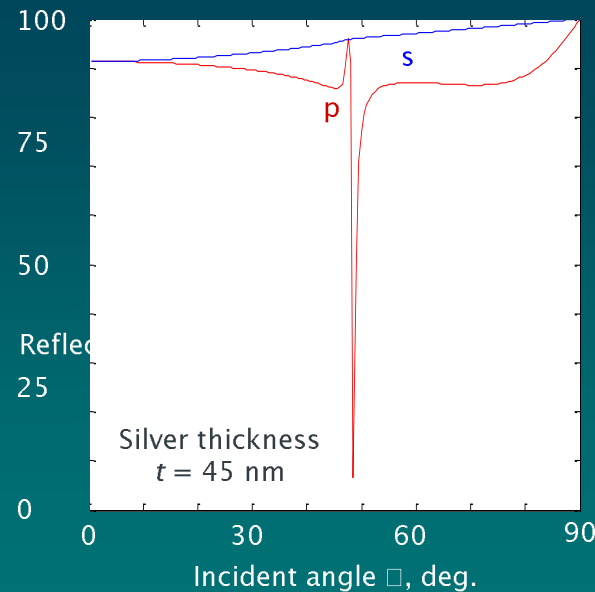
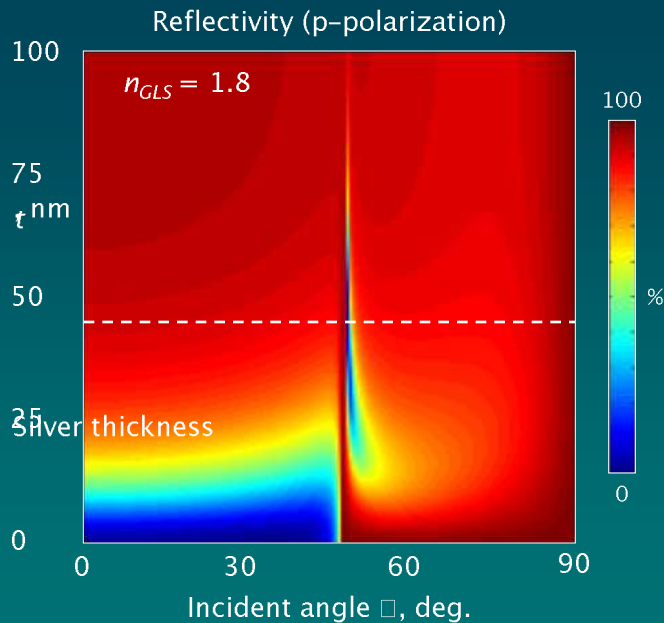
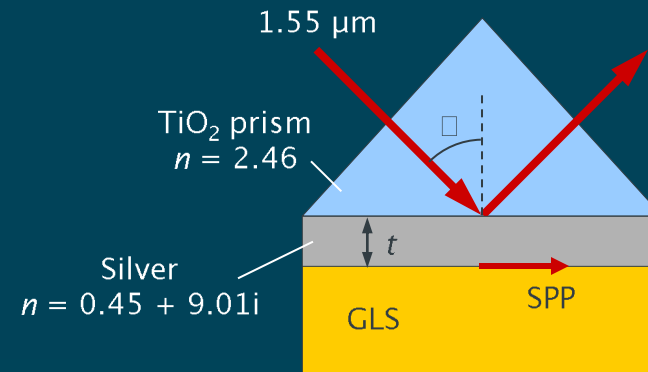
- high index
- highly absorbing)

Ga-La-S is much better:

- transparent above  $\sim 700$  nm
- High damage threshold
- Easily polished and coated
- non-toxic

UNIVERSITY OF  
**Southampton**

Optoelectronics  
Research Centre

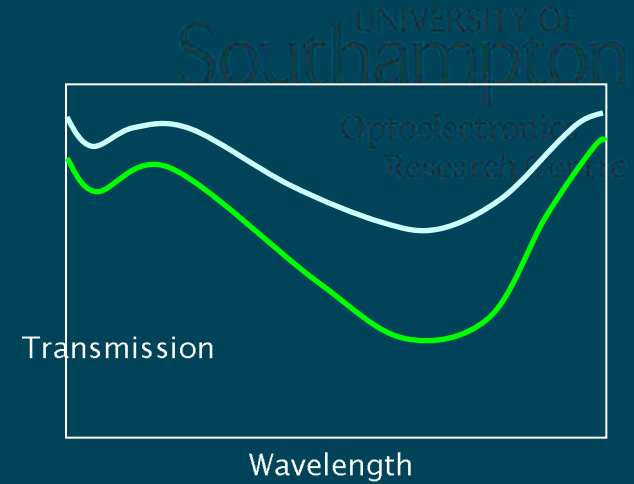
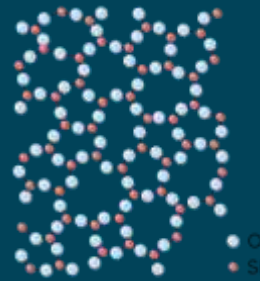


Light

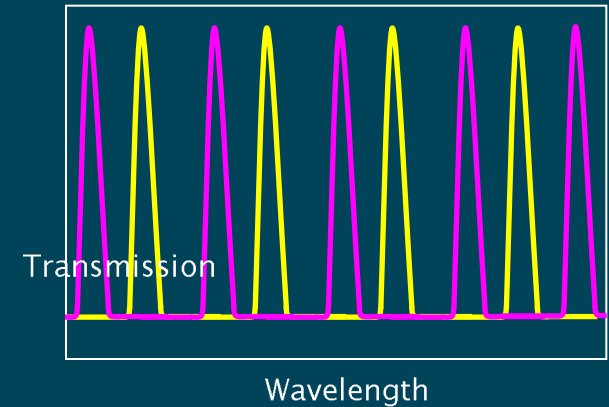
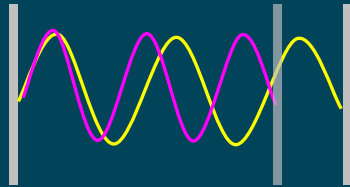


# Resonance switching

Nonlinear Medium

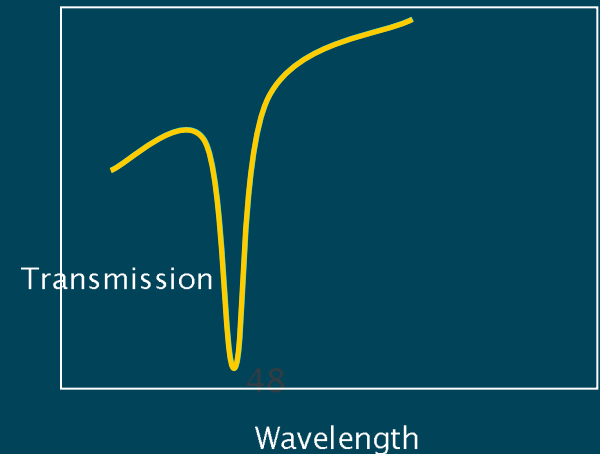
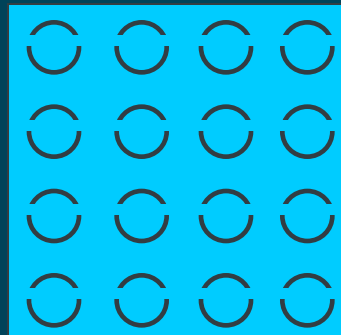


Fabry-Perot Resonator



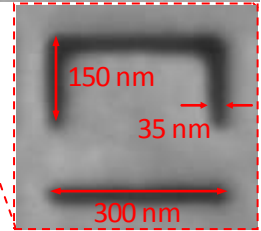
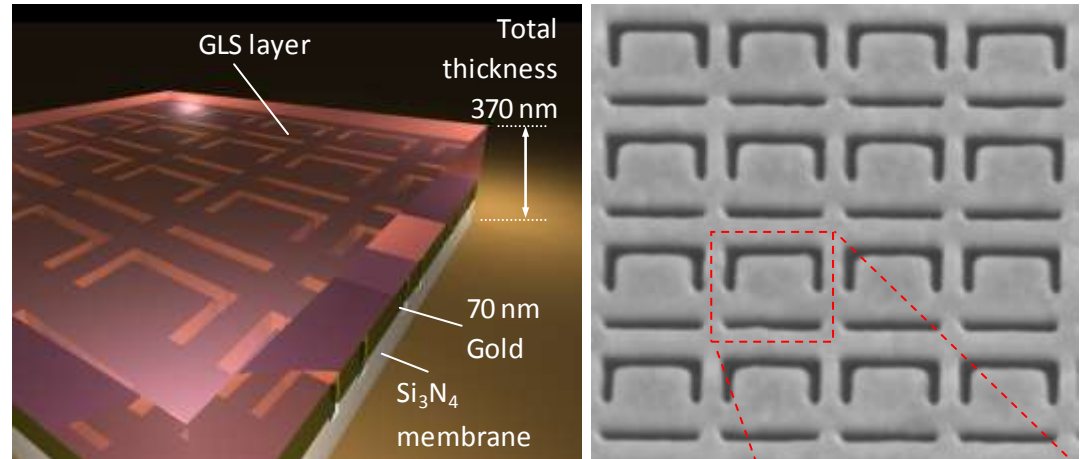
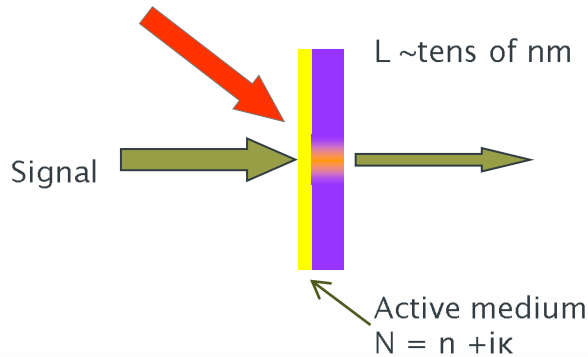
Can we switch our metamaterials?

Planar Metamaterial



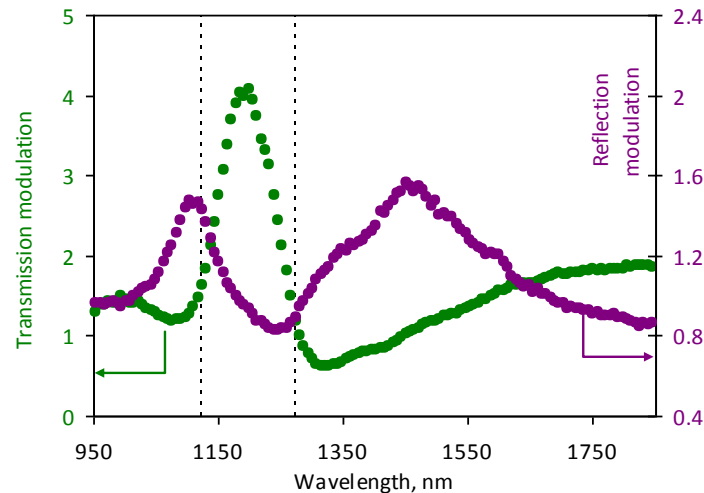
# Chalcogenide metamaterial hybrid Electro-optic modulator

Control  
(Induces change  $\Delta n$  and/or  $\Delta k$ )



## Gallium Lanthanum Sulphide:

- Optically/electrically-induced threshold switching: amorphous – crystalline
- Transmission contrast 4:1 in a device only  $1/3$  of a wavelength thick.
- Operational band tuneable by design across VIS-IR range



# Concluding Remarks

- Purify, purify, purify
- Don't (always) blame the composition
- Consider other geometries, emerging technologies
- Collaborate openly\* (or find a very wealthy sponsor)
- Learn from history



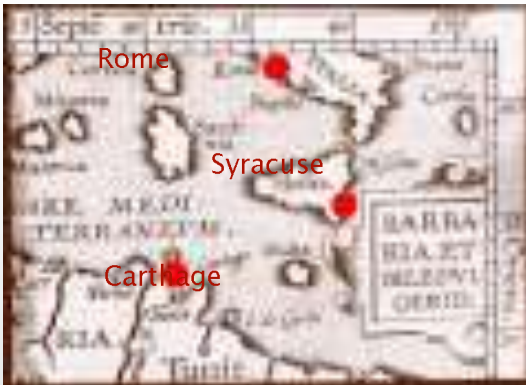
Four years later....

\*when you can



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