Govind P Kothiyal

Former Head, Glass & Advanced Ceramics Division
Chairman MRSI-Mumbai Chapter & Subject Group: Ceramics & Glasses
C/O Materials Group, Bhabha Atomic Research Centre,
Mumbai-400 085, India

Fields of Interest/Specialization:

- **Special glasses and glass ceramics**
  (Preparation and characterisation - thermo-physical-electrical, optical,sealing, biocompatibility, corrosion properties)
- **Thin crystalline and amorphous films**
  (Metallic, Semiconductor and insulating materials by conventional and Molecular beam epitaxy,characterisation for electrical,optical, structural & other properties)
- **Bulk single crystal growth**
  (Crystal growth by melt and vapour techniques and characterisation for structural, opto-electronic, optical, electrical and other properties)

Research publications: >250

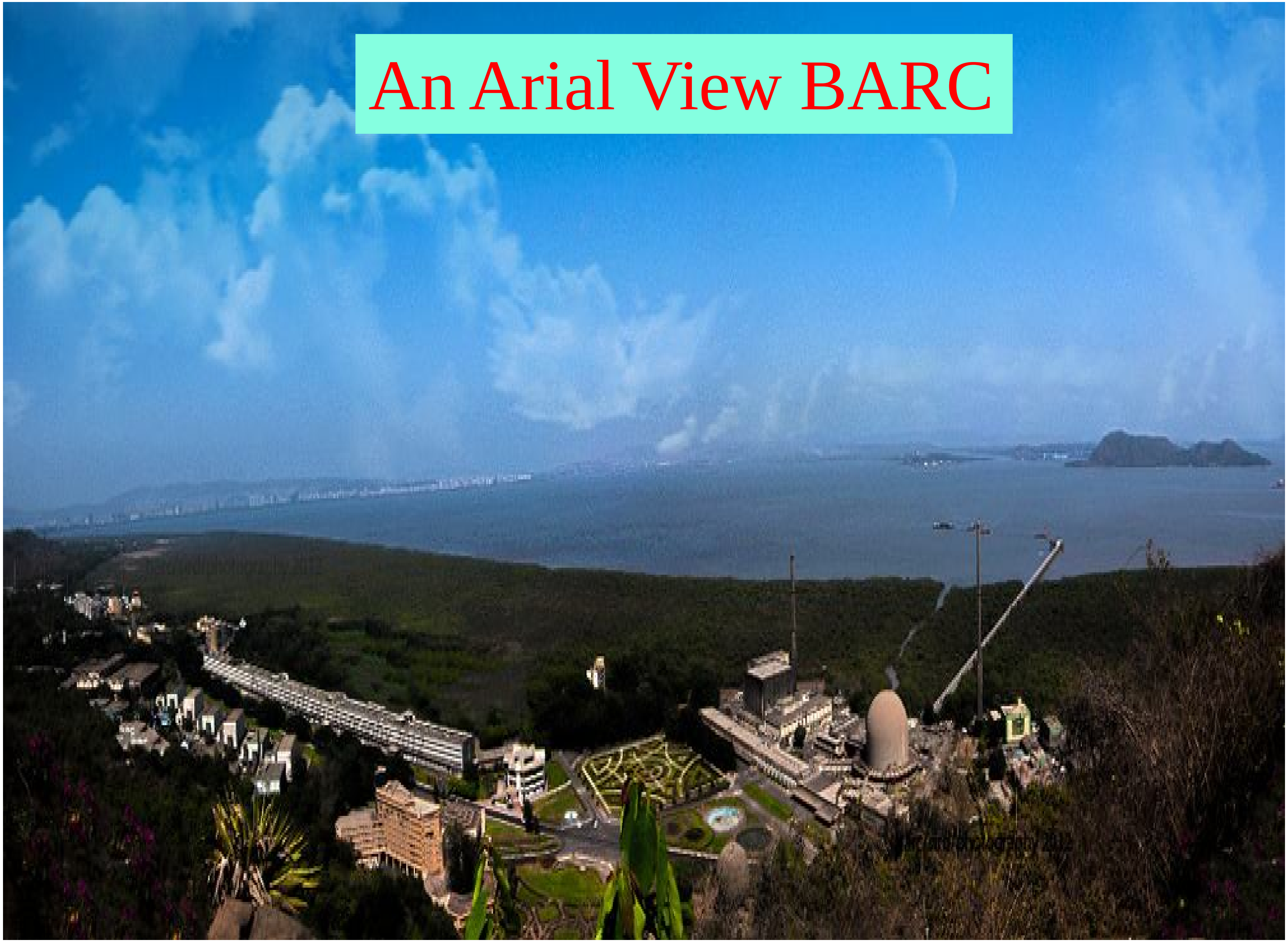
AWARDS:
Materials Research Society of India, (MRSI) Medal Lecture award (2003)., IFCPAR Project 2009-2012
Visiting Fellow, Department of Electrical Engineering and Computer Science, University of Michigan, USA (86-87)
Visiting Professor, University of Science & Technology Lille, France (Feb.-April 2007), INS Science Communication Award-2009 ; DAE Group Achievement Awards (2009,2011)

SOME ACTIVITIES ON FUNCTIONAL GLASS, GLASS-CRAMICS IN BARC/DAE

G.P.Kothiyal

Former Head Glass & Advanced Ceramics Division, Materials Group
Bhabha Atomic Research Centre, Mumbai.

An Arial View BARC



GLASS AND CERAMICS TECHNOLOGY LABORATORY, BARC

ACTIVITIES ON GLASS & GLASS-CERAMICS IN BARC/DAE

MAJOR AREAS FOR R&D

- Functional Glass and Glass ceramics:
  (***Sealants, biomaterials, machinable ceramics, transparent GC)***
- Matrices for radioactive waste:
- Metallic Glasses :
- Laser Glass:
- Radiation Shielding Windows:

Some developments related to Glass/Glass-ceramics & Ceramics

•Technology Development

- Glass-to-metal seals
- Ceramic-to-metal seals(conventional and Active alloy Brazing), Glass-ceramic to –metal seals

• Materials Development

- **Glasses (Oxides/ non-oxides)**
  - **Oxides (Lead silicate, borosilicate, sodium aluminum phosphate etc.) for low temperature sealants for different metals**
  - **Non Oxides (Arsenic & antimony chalcogenides) for Infrared windows**
- Glass-ceramics(GCs)
  - **Magnesium-Aluminium-Silicate (MAS) machinable GC**
  - **Lithium-Zinc-Silicate (LZS) & Lithium Aluminum Silicate for seals**

•**High temperature sealant materials for possible use in SOFC energy conversion devices**

•$BaO\text{-}ZnO/MgO\text{-}SiO_2$, $BaO\text{-}Al_2O_3\text{-}La_2O_3\text{-}B_2O_3\text{-}SiO_2$
$BaO\text{-}CaO\text{-}Al_2O_3\text{-}B_2O_3\text{-}SiO_2$

Users: DAE (HWPs, BARC), ISRO, DRDO

Brief Introduction

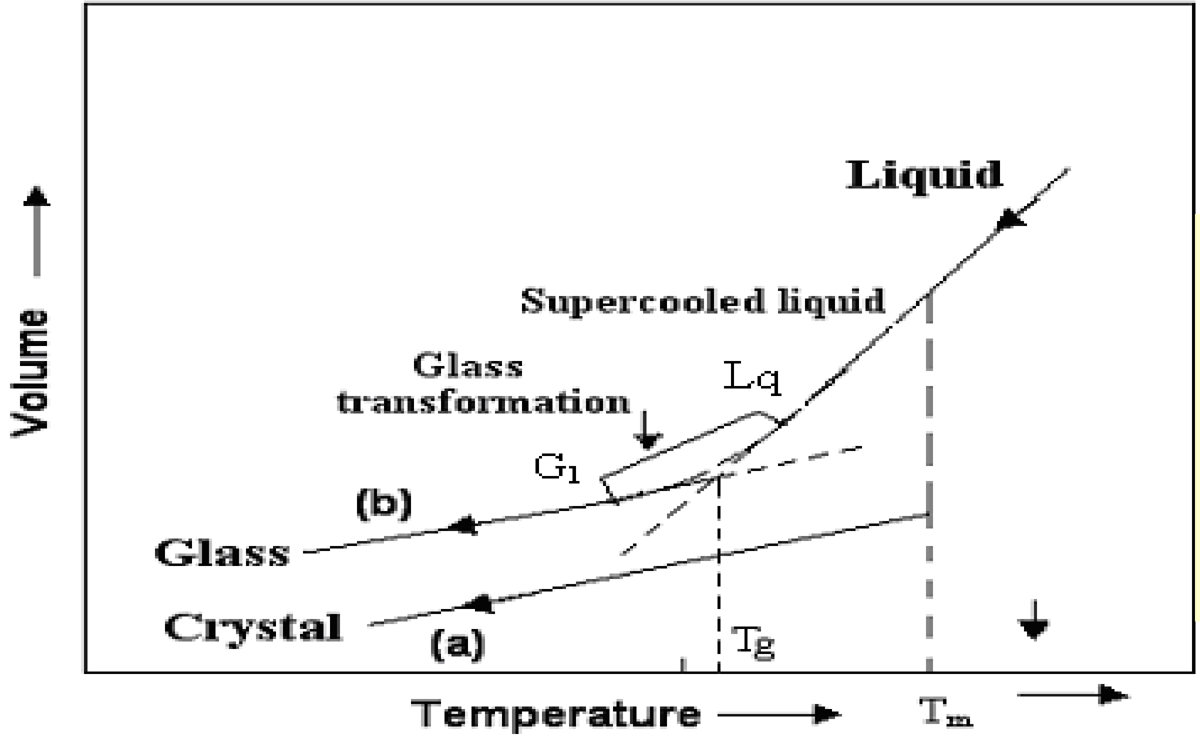
Glass

Glass is a class of an amorphous solid completely lacking in long-range order and which at least exhibits glass transition behaviour.

Glass – ceramic

Glass-ceramics are composed of crystalline grains immersed in glassy matrix, prepared by controlled crystallization of base glasses with suitable nucleating agent(MgF_2, P_2O_5 , TiO_2 , ZrO_2)

For preparation of the glass-ceramics, nucleation and crystallization steps are crucial.



Variation of specific volume of a melt as a function of Temp. when being cooled at different rates (q)

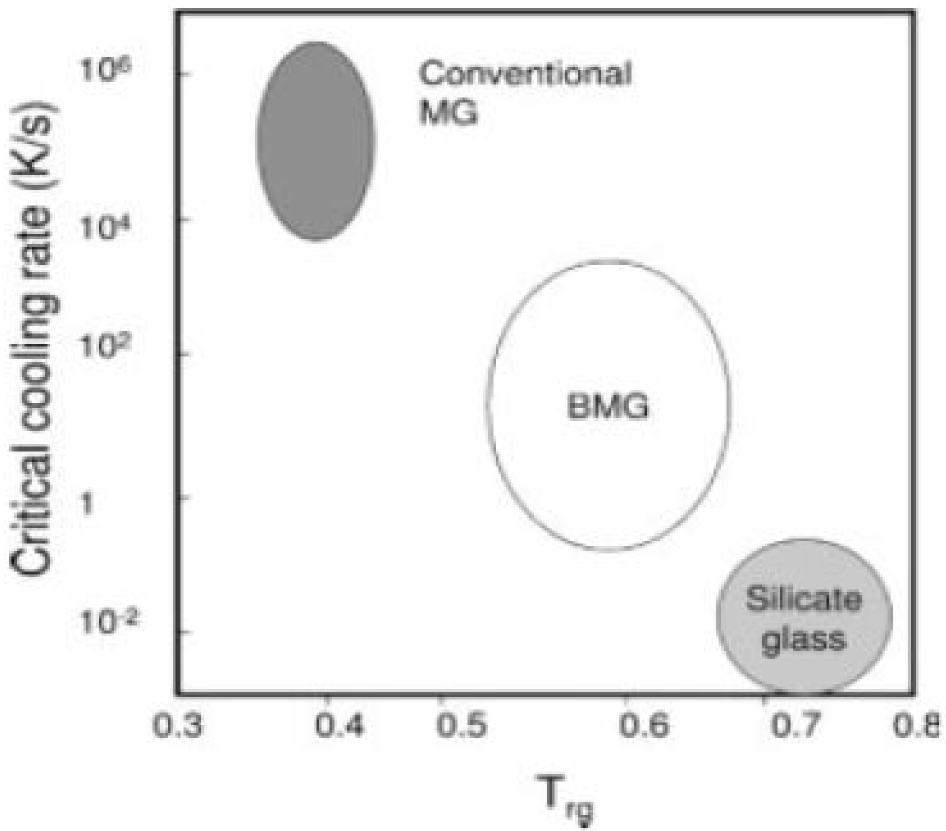
$$q = q_o e^{-\frac{1}{c}\left(\frac{1}{T_g}-\frac{1}{T_m}\right)}$$

$$K_g = \frac{T_c - T_g}{T_m - T_c}$$

When $(T_c – T_g)$ is large, $(T_m - T_c)$ is small, Process of nucleation & crystallization is not strong :

Glass-forming tendency **Kg** is high.

Critical cooling rates for different classes of glass as a function of reduced (T_g) glass transition temp. $T_{rg} = T_g/T_m$ T_m-melting temp.

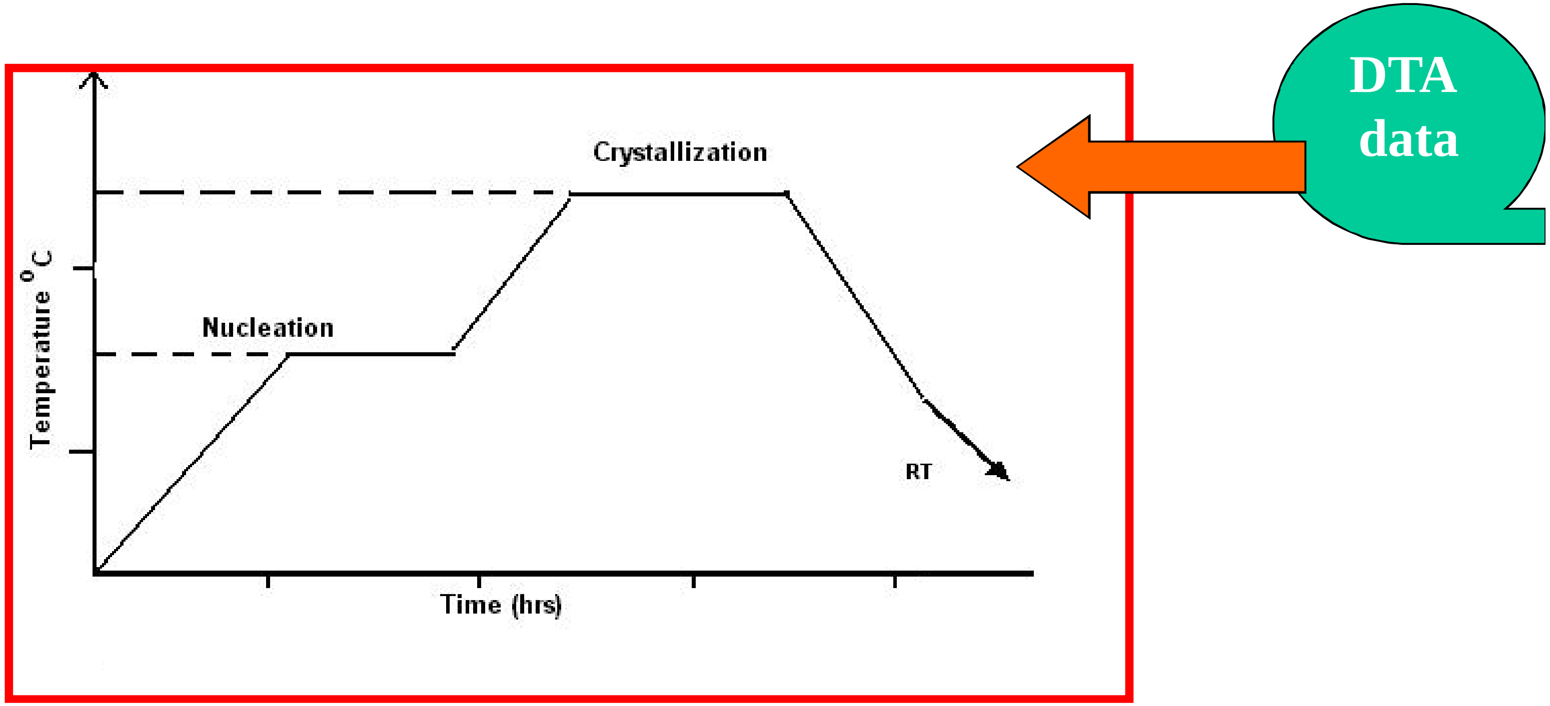


Preparation of Glass-ceramics

- **Glass Preparation**

Melt-quenched technique ⟶ Annealing

- **Controlled crystallization of base glass**



Heat schedule for conversion of glass to glass-ceramics

Formation of Glass-ceramics

BARC
आभा परमाणु अनुसंधान केंद्र
BHABHA ATOMIC RESEARCH CENTRE

- A variety of micro-structural configurations can be formed:
- Composition control and thermal treatment.
- Either surface nucleation/crystallization or internal nucleation or a combination of both to design glass-ceramics of the desired properties.
- For glass-ceramics based on internal nucleation and growth, a general evolution pattern is observed in crystallization cycle:
- Amorphous phase separation and/or precipitation of primary crystalline nuclei, nucleation and growth of meta stable crystalline phases and approach to stable crystalline assemblage.
- **Unique micro-structures, most of which can not be duplicated by other ceramic processes, can be produced by interrupting the cycle at a desired point**

IMPORTANT PROPERTIES OF GLASS-CERAMICS

In comparison to parent glasses:

- ☞ **Exhibit better thermal stability**
- ☞ **Superior electrical insulation**
- ☞ **Higher mechanical strength**
- ☞ **Thermal expansion co-efficient tunability**

Some Technological Applications of Glass Ceramics

Electronics & Optoelectronics: Photomachineable Circuit Board, Capacitors, Insulators, Power Packaging , Laser Rods, Transparent Optical Windows, Radiation Resistance Windows

Military: Radomes, Ceramics Seals for Bomb Trigger

Vacuum Technology: Ceramics to Metal Seals for Vacuum Devices and Energy sources like SOFC

Domestic: Cooking Ware, Table Ware, Heating Surfaces

Chemical Industrial: Corrosion Resistant Tubing, Pump Impellor, Telescope Mirror Blank, Radioactive waste immobilisation,

Biological: Implants and Implants Coatings, Dental Materials

What is Functionality?

- Broadly speaking functional glasses/glass-ceramics, are materials possessing certain useful combinations of properties, which make them suitable for specific applications .
- Definition is by no means unique, but gives an idea what a functional material is supposed to be.
- Functionalization of a material needs a thorough understanding of various properties including structure property correlations.

⇨ *Functionality can be optical, thermo-physical, magnetic, chemical, biological, tribological & so on and a combination of these.*

WORK AT GCTL, BARC:
Sealants for High Temperature applications

Base composition:

- √ : **BaO- CaO -Al_2O_3- B_2O_3-SiO_2 (BCABS);Additives-P_2O_5, TiO_2, Cr_2O_5**
- √: **(51-x) BaO-9.0ZnO-(40-y)SiO_2- y(additive)-xB_2O_3(BZS)**
- √ : **51SrO-9ZnO (40-x) SiO_2 , Additive x= B_2O_3, Al_2O_3, V_2O_5 &Cr_2O_3 (SZS)**
- √: 30BaO-20SrO--10 Al_2O_3- (40-x) SiO_2 -xCr_2O_3, x= 0, and 2 mole% **(BSAS)**
- √ : **xSrO-(50-x)MgO-4B_2O_3-35SiO_2--6Al_2O_3-5P_2O_5,where $0 \leq x \leq 50$ mol.%**

Preparation: **Melt-quench followed by controlled crystallization based on DTA data**

Characterization: **XRD, Thermo-mechanical , Structural (SEM, FTIR, Raman, MAS-NMR), Electrical properties, wetting, Hermeticity (Room and high temperature) etc.**

What Are Important parameters related to seals?

- Hermeticity
- Operating temperature (High for SOFC)
- Mechanical strength
- Pressure load capacity
- Solderabilty
- Corrosion resistance /Long term stability
- Insulation resistance
- Flash over voltage
- Current carrying capacity

......Depending upon applications

What we look for glass/glass-ceramics sealing?

- Matched thermal expansion coefficient
- Sealing temperature
- Low viscosity
- Good wettability
- Good chemical bonding
- No undesired chemical reaction (Of great concern for SOFC application)
- Acceptable chemical, mechanical and electrical properties

Glass Seal

BARC
आभा परमाणु अनुसंधान केंद्र
BHABHA ATOMIC RESEARCH CENTRE

Requirements for Suitable Glass Seals

- No chemical reaction with the joining components and stability in oxidizing and wet reducing atmospheres
- Viscosity: 10^5 Pa.s at joining temperature (1000^{o}C) and >10^9 Pa.s at operating temperature (850^{o}C)
- Small thermal expansion mismatch with respect to SOFC components (TEC = 10-13 x10^{-6} K^{-1})
- Leak rate less than 10^{-7} mbar l $s^{-1}$$cm^{-1}$
- Resistivity more than 2 kΩ cm

Sealant

Working Environment of a Sealant for SOFC

- An average temperature of 750°C
- Continuous exposure to oxidizing atmosphere on cathode side ($p_{O2} = 2x10^4$ Pa) and reducing atmosphere on anode side ($p_{O2} = 1 \times 10^{-13}$ Pa)
- The device lifetime is anticipated to be > 10,000 hours

Glass Seal

Challenges to Glass Seals

- Brittle nature of glasses below the glass transition temperature
- Reaction with other cell components, such as electrodes, interconnect, electrolyte at SOFC operating temperatures
- Fracture under pressure
- Failure due to rapid thermal cycling
- Failure upon thermal aging

but

Glass-ceramic seals may ease the situation

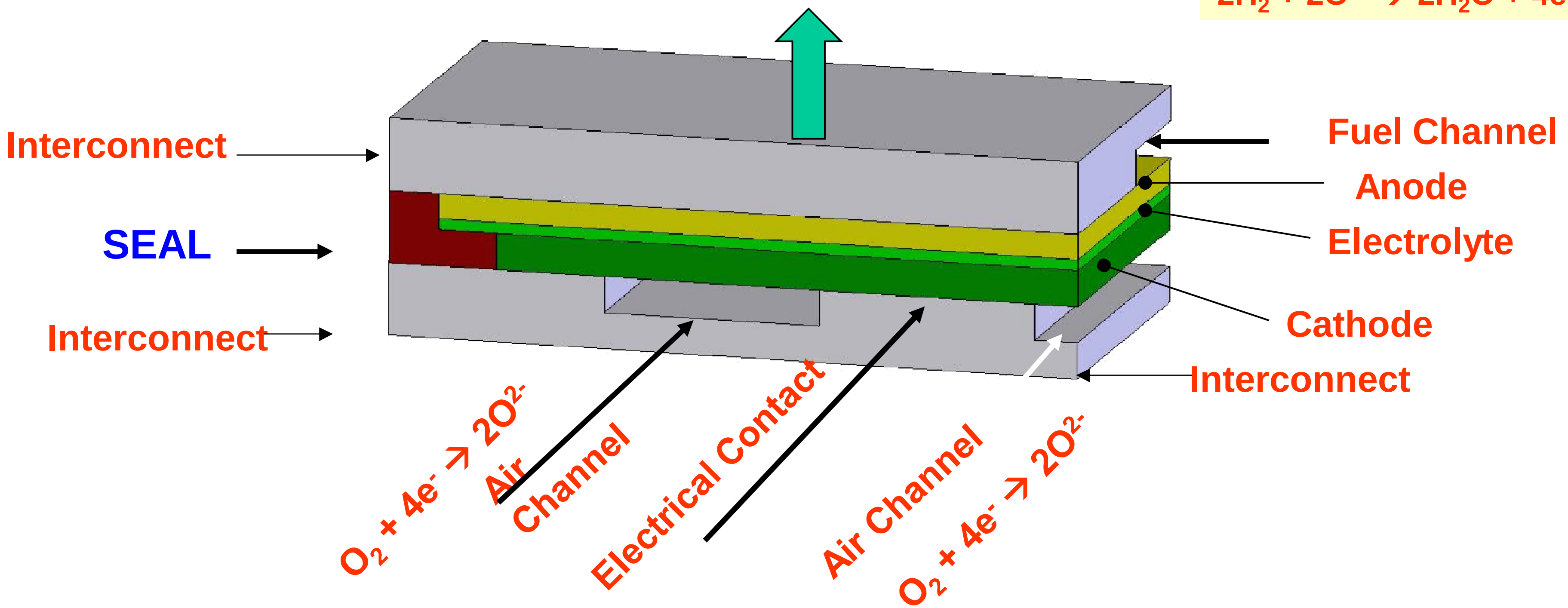
Sealant

Purpose of Sealing Material

- Prevents fuel leakage and air mixing at high temperature
- Seals the electrolyte against the interconnect (ceramic or alloy) of the device

$2CO + 2O^{2-} \rightarrow 2CO_2 + 4e^-$

$2H_2 + 2O^{2-} \rightarrow 2H_2O + 4e^-$



CHALLENGES

Mechanical

- TEC matching
- Acceptable bond strength
- Resistant to degradation due to thermal cycling/thermal shock

Design/fabrication

- Low cost
- Acceptable sealing environment /temperature
- Design flexibility

Chemical

- chemical stability under oxidizing/wet fuel environments
- Long-term chemical compatibility with the adjacent sealing surfaces

Electrical

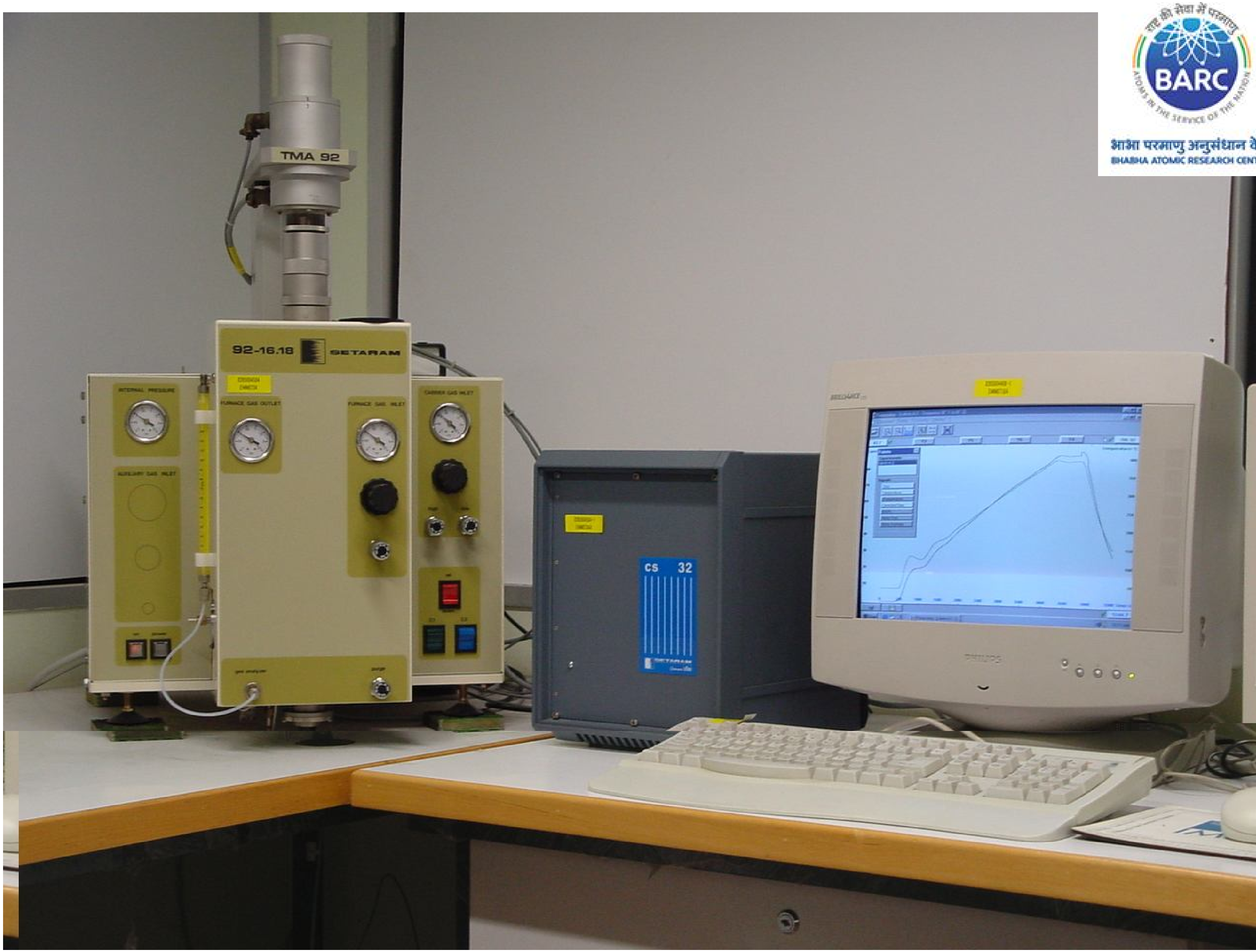
- Non-conductive

(non-shorting configuration)

Pouring of glass melt at 1550^{O}C from a lowering and raising hearth type furnace and annealing at 500^{o}C

GACD

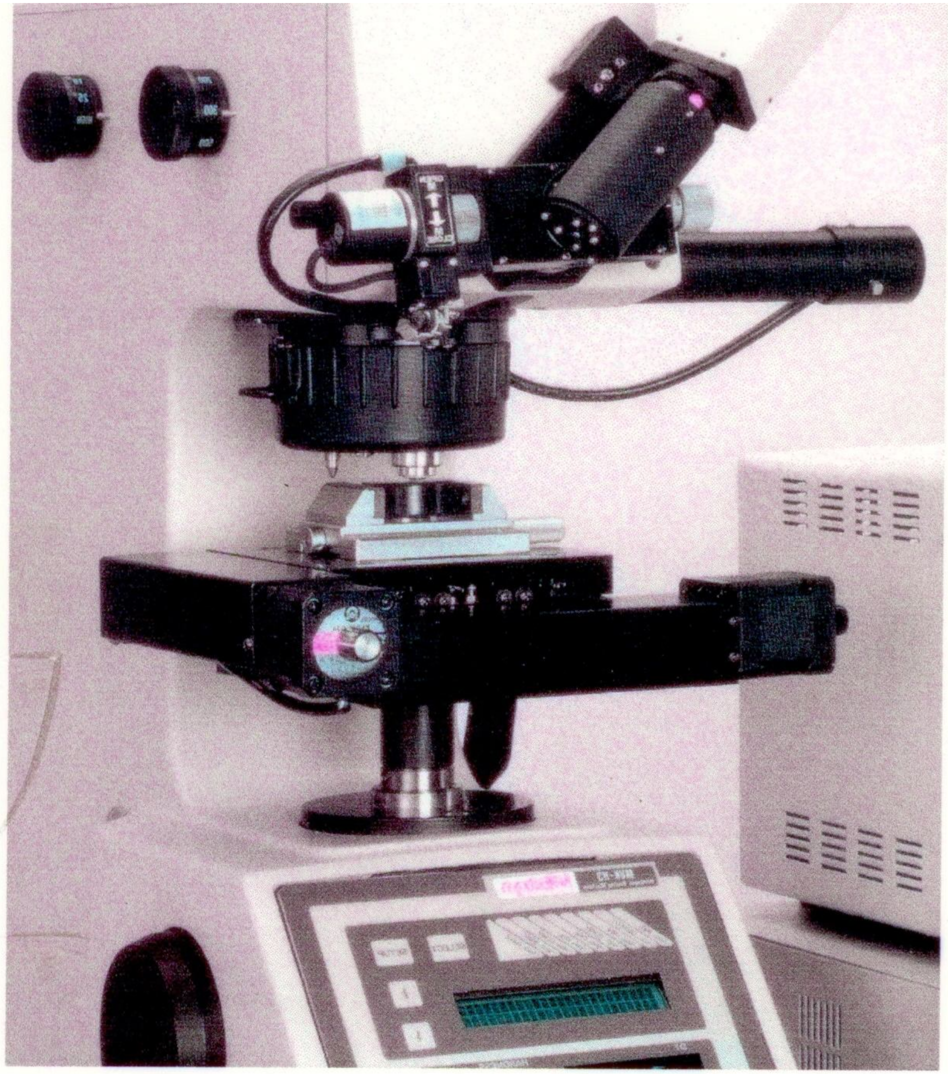
Horizontal sliding annealing furnace for easy pouring and annealing at high temperature under different ambients.



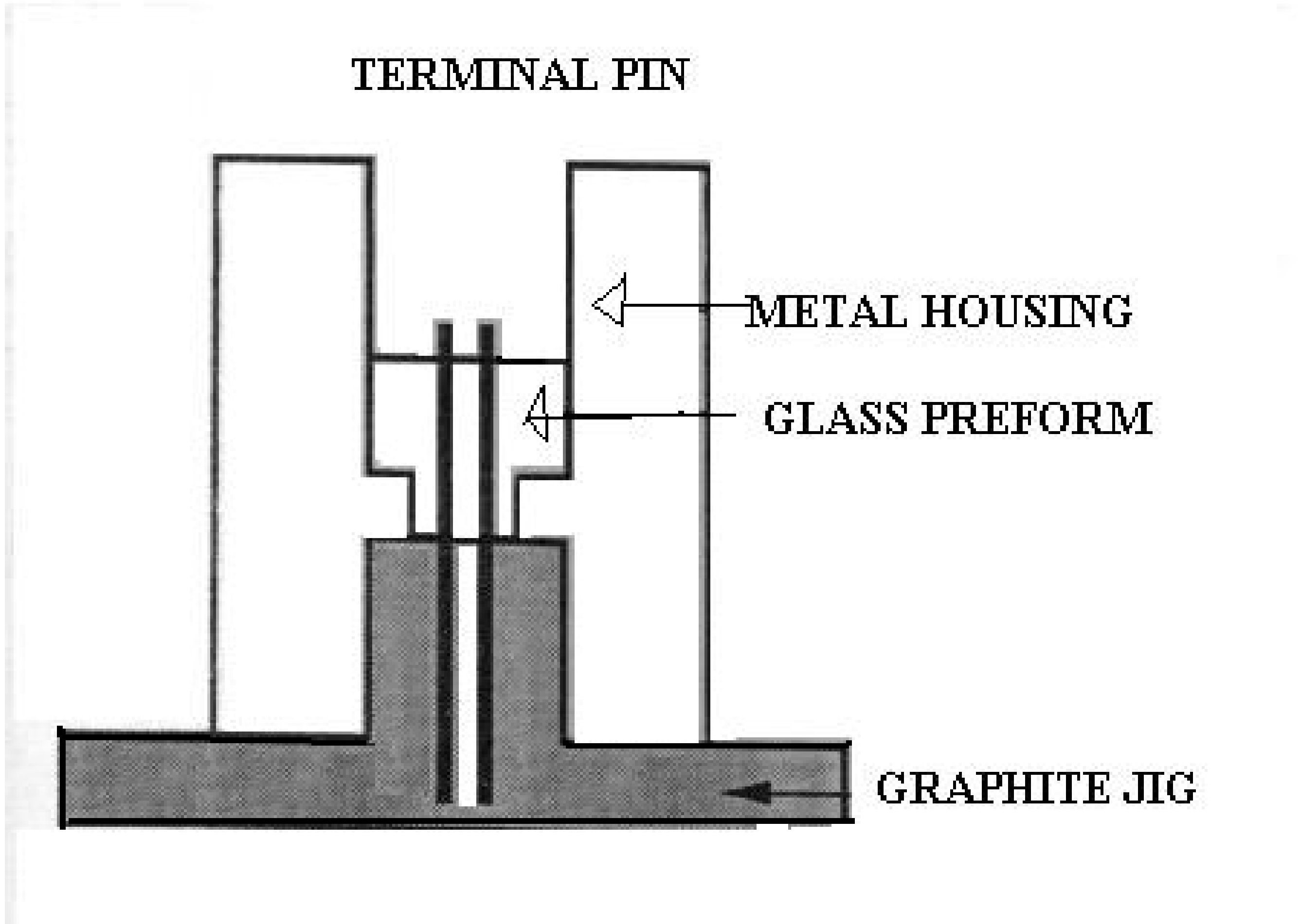
भाभा परमाणु अनुसंधान केंद्र
BHABHA ATOMIC RESEARCH CENTRE

Characterizaton

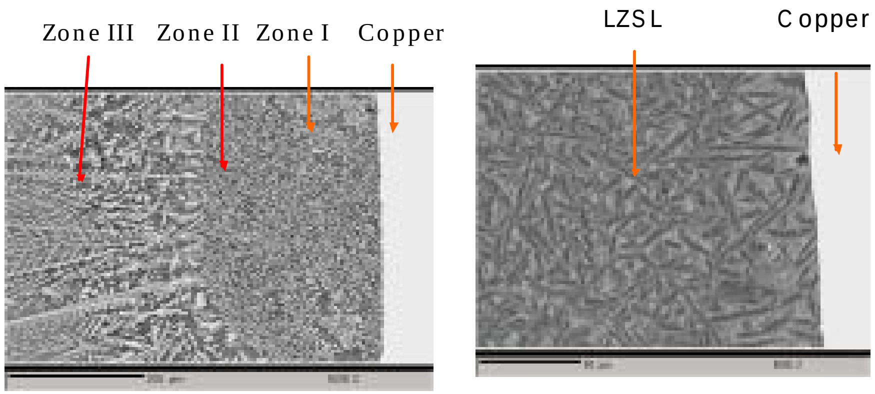
- **Micro hardness : Vicker's Indentation technique using M/s. Leico,VMHT30**
- **Load 50-100 gm**
- **Dwell: 5-10 sec**



Schematic representation of preparation of an electrical feedthrough

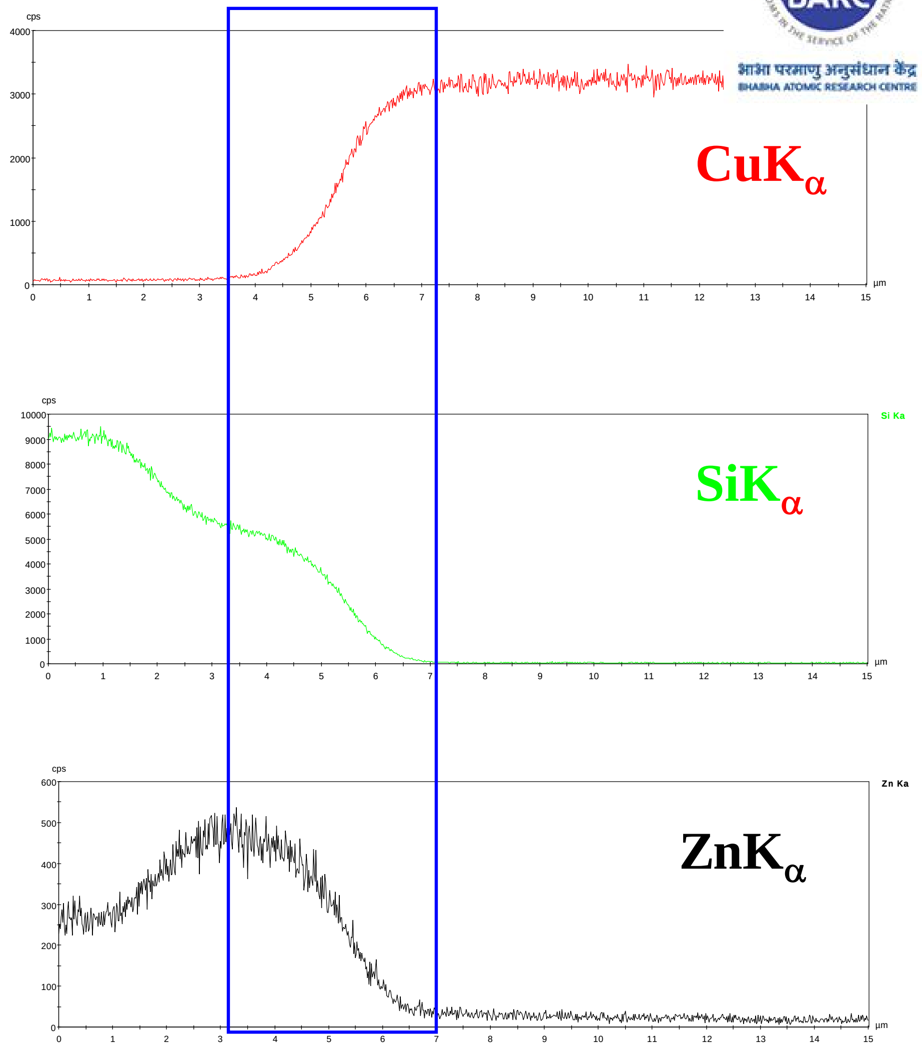


LZS Glass –ceramic- to- SS and- Cu seals



LZS glass-ceramic/Cu interface

Microstructure(BSE Image)



Line scans of elements across the Cu to glass-ceramic (LZSH)

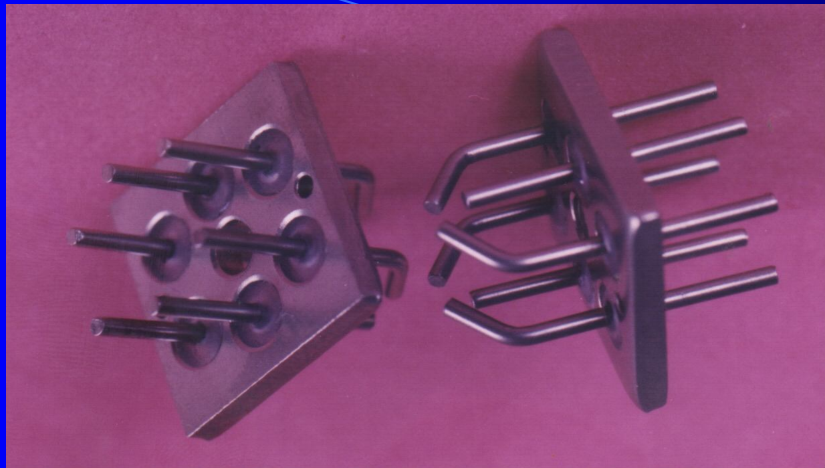
Mater.Lett.58(2004)2423, J. Solid State Chem. 181(2008)269, J. Mater Sc.44(2009)3349

Seal For High Pressure Application

Lithium Aluminum Silicate (LAS)

- He leak rate 10^{-9}Torr l/s at a Vacuum ~10^{-6}Torr
- Withstands high pressures of 12,000 psi
- Resistant to highly corrosive alkaline ambient of liquid ammonia and potassium amide

J Solid State Chem., 183(2010)1416-1422



Triple filament seal

Seven pin seal

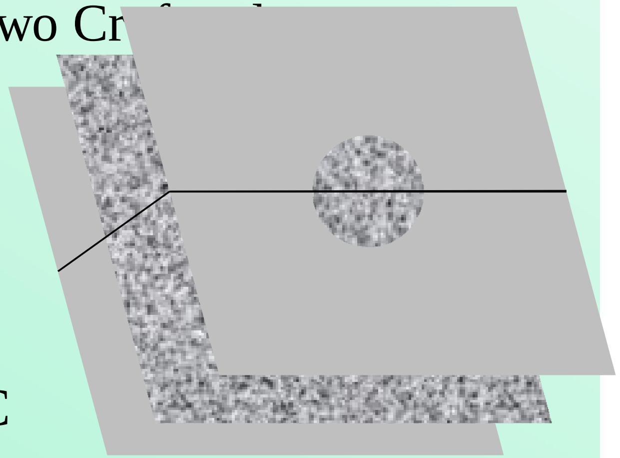
Triple filament seals Mass Spectrometers and 7-pin-Glass-to-metal seals for HWPs

Thermo-mechanical parameters for BCABS samples with various additives.

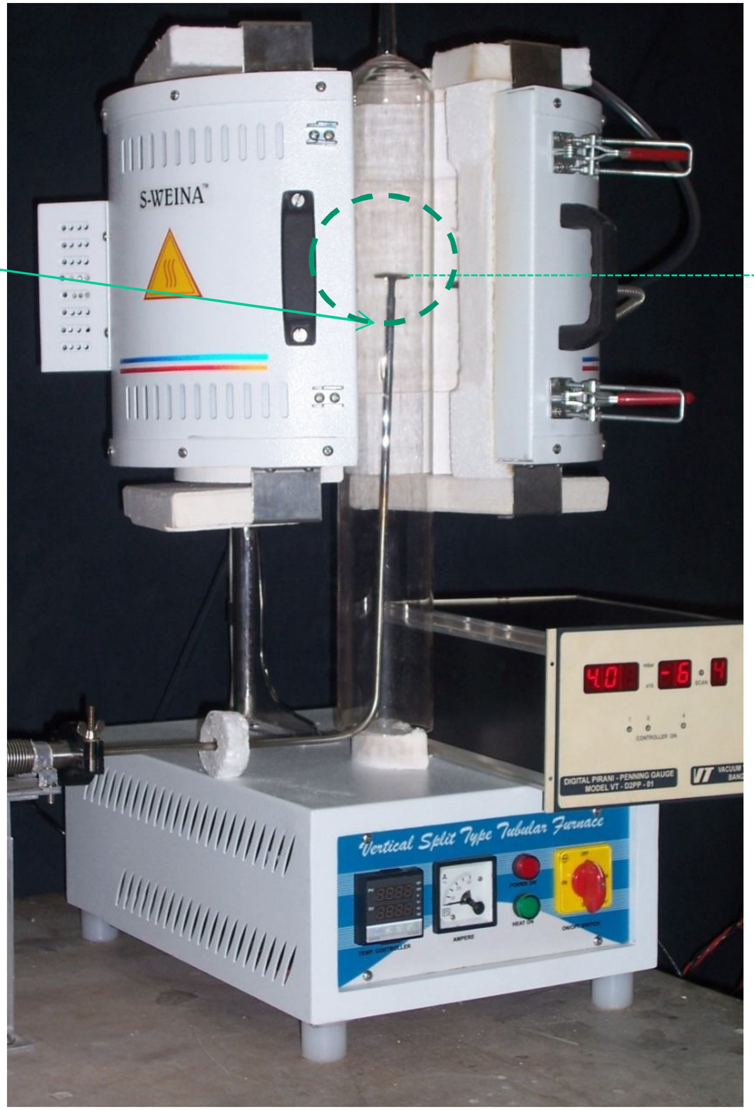
Samples	TEC (30-300) x $10^{-6}/^oC$	T_g (^oC)	T_d (^oC)	Microhardness (GPa)
BCABS (No additive)	11.7	619	665	5.68
BCABST(TiO_2)	11.34	629	669	5.60
BCABSP(P_2O_5)	11.85	641	660	5.39
BCABSZ(ZrO_2)	12.81	652	670	5.74
BCABSCr(Cr_2O_3)	10.59	638	678	--

High temperature Seals fabrication

Glass powders	made by milling
Geometry	sandwiched type between two Cr
	(15mm × 15mm)
Sealing temp.	~990^{o}C
Vacuum integrity	at room temperature
Thermal cycles	up to 1000 -1500h at 800^{o}C



For characterization	polished cross-section of the seals after heat treatment at 800^{o}C
	microstructure and inter-diffusion of elements at the interface using SEM with EDS

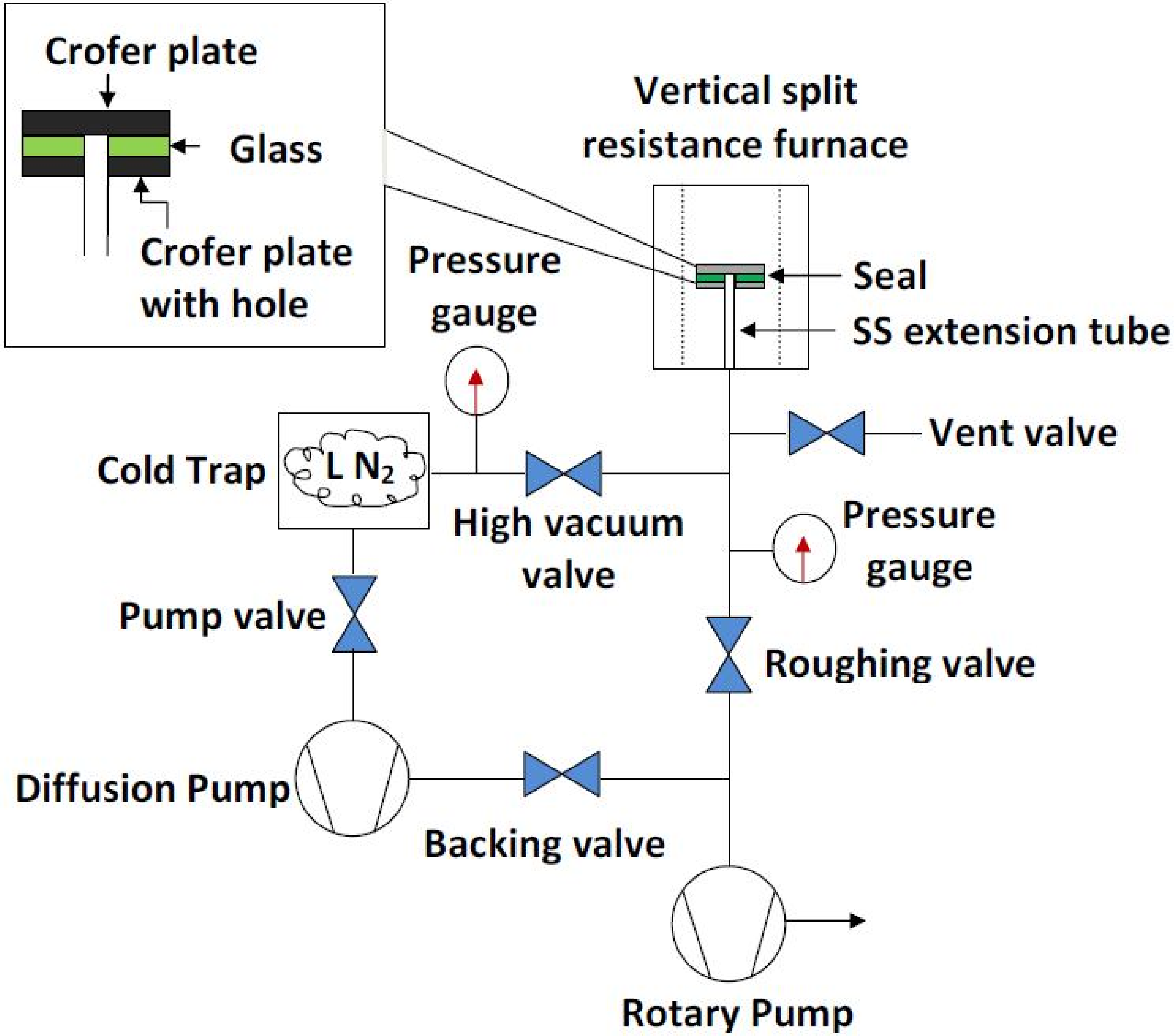


Sample holder

BCABST-to-Crofer22 seal

To vacuum pump

In-house developed high temperature (upto 800^{o}C) leak testing setup.



Schematic of leak testing set up for high temperature

Glass compositions prepared for Studying effect of P_2O_5

Component	Fractions (mol%)
BaO	35
CaO	15
Al_2O_3	5
SiO_2	37-x
B_2O_3	8
Cr_2O_3	-
P_2O_5	x^*
$Ba_3(PO_4)_2$	

Under IFCPAR-Project 4008-1

Tabulated TEC, Tg and Tds for glasses

Name	TEC (ppm) (150-500)	Tg	Tds
BCABS-0P	11.8	635	674
BCABS-1P	11.6	638	673
BCABS-2P	11.5	641	675
BCABS-3P	11.4	642	677
BCABS-4P	11.2	646	677
BCABS-5P	9.9	653	683

All Tg values agree well with the DTA results. DTA shows a weak crystallization exotherm at 730^{o}C

Conclusion

- Addition of P_2O_5 increases network polymerization
- This is caused by removal of modifier cations to charge compensate PO_4^-
- The addition of P_2O_5 increases crystallization tendency at high temperature
- This coupled with increased flow temperature can make sealing difficult.
- It was concluded that<2mol% of P_2O_5 could be added with improved bonding properties.

Composition: (mol%) 30SiO_2-20SrO-30BaO-10B_2O_3-5La_2O_3

System is of particular interest as replacing BaO with SrO mitigates formation of $BaCrO_4$.
This we may induce the formation of $SrAl_2Si_2O_8$, which has higher TEC than $BaAl_2Si_2O_8$.

- ❑ Originality lies in the combined addition of BaO and P_2O_5 to tailor the sealing and thermo physical properties of the sealants.

The aim is to keep a moderate sealing temperature and to control crystallization in glasses.
The glasses have been formulated by addition of $Ba_3(PO_4)_2$ to a base glass composition (BASP0).
•It is expected that network polymerization will not be affected.

Table : Composition (in mol%)

Sample	SiO_2	SrO	BaO	La_2O_3	Al_2O_3	B_2O_3	P_2O_5
BASP0	30	20	30	5	5	10	0
BASP1	28.8	19.2	31.7	4.8	4.8	9.6	0.9
BASP2	27.7	18.5	33.3	9.2	4.6	4.6	1.8

- Glasses are prepared by melt-quench technique.
- Bubble-free and transparent glasses are obtained.
- These have been formulated by addition of $Ba_3(PO_4)_2$ to a base glass composition (BASP0)

TMA data

Sample	TEC ($\pm$ 0.1x10^{-6} K^{-1})			Tg ($\pm$ 2°C)
	Base glass	after 6h at 800°C	after 100h at 800°C	
BASP0	11.4	12.2	12.4	650
BASP1	12	12	12.5	592
BASP2	13	13	12.1	584

- **TEC values of as prepared glass are in good match with that of Croffer-22**
- **TEC values show good thermal stability**
- **The glass transition temperature has decreased from 650°C to 584°C**

MACHINABLE GLASS-CERAMICS

Magnesium aluminium silicate (MAS) machinable glass-ceramics is another development for high voltage and ultra high vacuum applications. Micro-structural studies have been carried out on these materials to understand structure property correlations

FLUOROPHLOGOPITE PHASE

K Al [Mg 3 Si 3O10] F2

Responsible for machinability

INITIAL CHARGE PREPARTION

Typical nominal composition of MAS samples (in mol %)

Batch No.	SiO_2	MgO	Al_2O_3	B_2O_3	K_2O	MgF_2
Sample# 1	52.8	21.4	7.58	6.82	6.88	4.4
Sample# 2	50.1	20.5	12.3	6.46	6.6	4.15
Sample# 3	48.6	19.9	14.7	6.22	6.42	4.08

CRYSTALLIZATION PROCESS

NUCLEATION AT ~600^{O}C
MgF_2 PHASE SEPARATION

↓

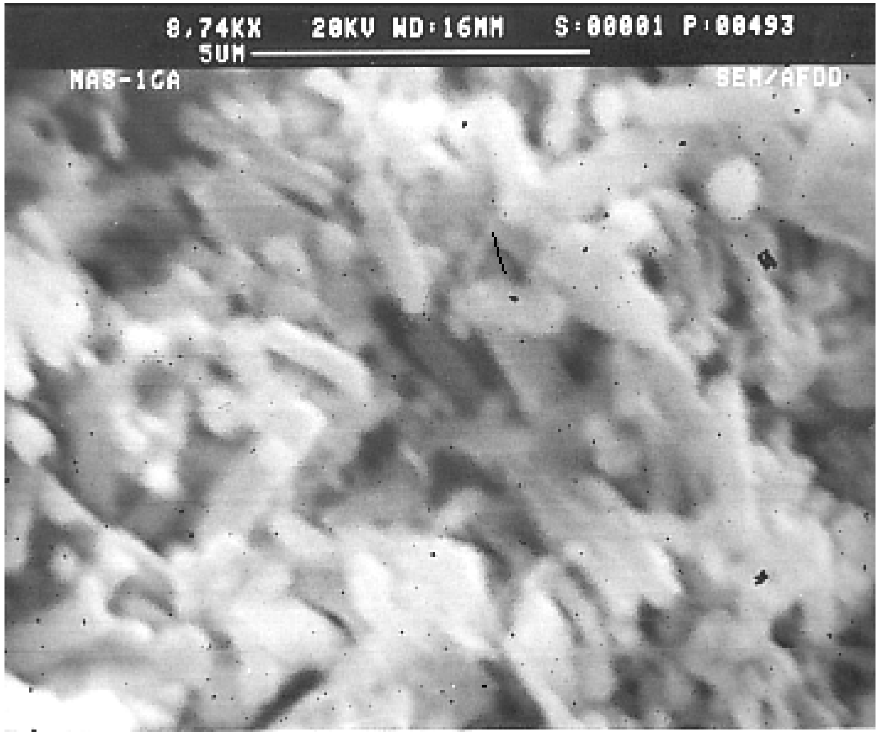
AT ~750^{O}C
NORBERGITE PHASE MgF_2. $MgSiO_4$

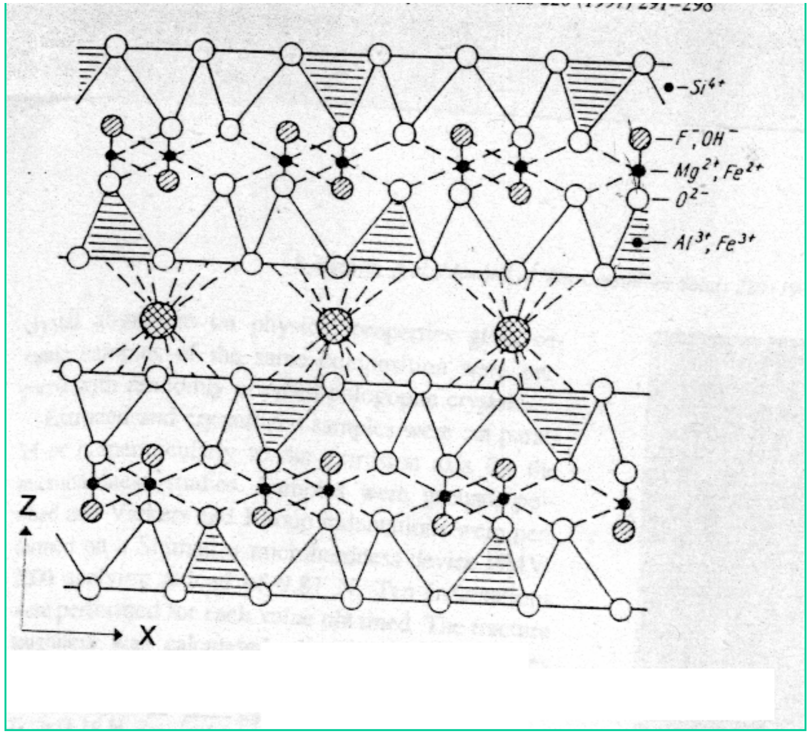
↓

AT ~850^{O}C
CHONDRODITE PHASE,
MgF_2.2$MgSiO_4$

↓

AT~ 950^{o}C
FLUOROPHLOGOPITE PHASE
K Al [Mg_3 Si_3O_{10}] F_2





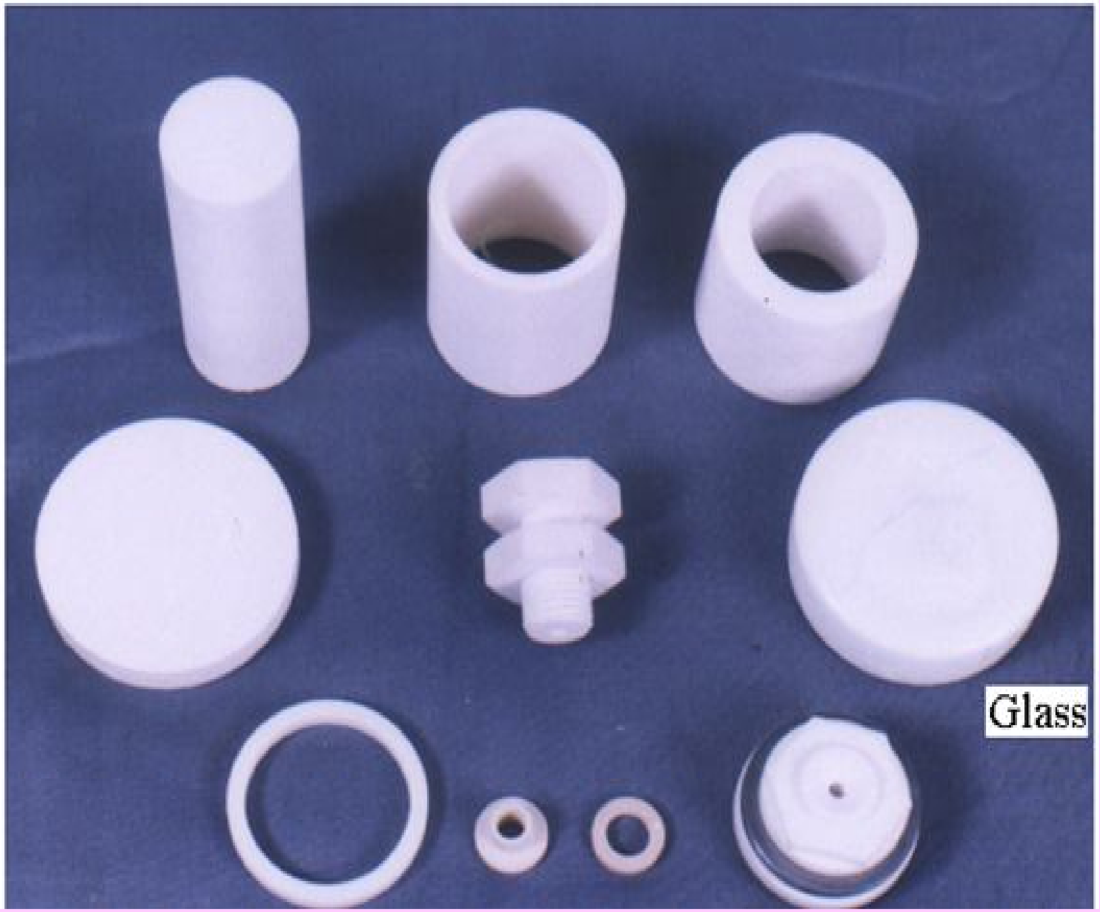
Microstructure of machinable MAS glass ceramics

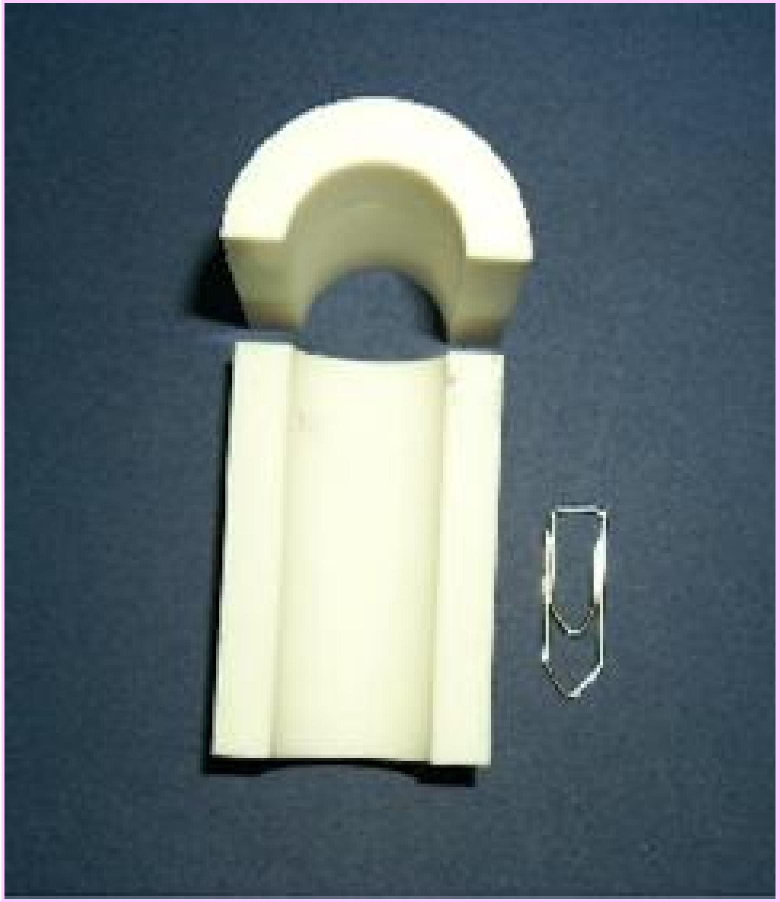
Crystal structure of (101)-plane of fluorophlogopite

2:1 negatively charged layer connected by positively charged inter layer alkai ions(Na^+ , K^+),

Each 2:1 sheet consist of two tetrahedral layer of composition T_2O_5 (1/2T = Al, 3/2T=Si) ; All octahedral sites are occupied by Mg^{+2}

Components fabricated from MAS glass-ceramics





- **Break down strength: 220 – 250 kV/ cm**
- **Micro-hardness: 2.5 GPa (under load of 50gms for 5 secs)**
- **Outgassing rate: 7.9 x 10^{-9} Torr. cm^{-2} sec^{-1}**
- **Thermal expansion coefficient: 9.8 x10^{-6} / ^{o}C (30 – 500 ^{o}C)**

G&ACD

Non-Oxide Glasses

- Preparation of chalcogenide $(As_2S_3)_{1-x}(Sb_2S_3)_x$ Glasses and studies on their structural, optical and thermo-mechanical Properties
- Structural Study of Chalcohalide Sb_2Se_3-CuI glass by neutron diffraction

Advantages of chalcogenide glasses

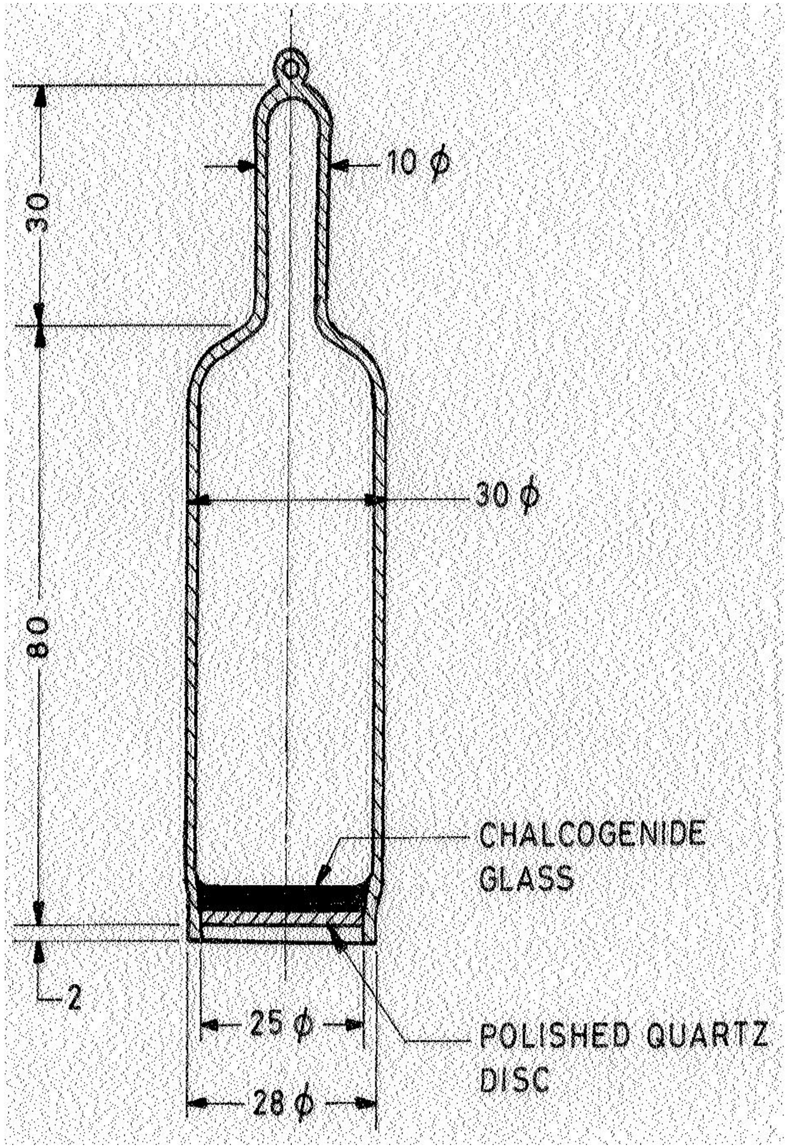
- Broad infra red light transparency
- Higher linear refractive index (RI>2.0) compared to silicate glasses (RI~1.5) (photonic crystals)
- Low phonon energy (up-conversion lasers)
- High optical nonlinearity (ultrafast all-optical switching, supercontinuum generation)

Important properties

Non hygroscopic, chemically stable, lesser prone to devitrification and high resistivity.
Offer more isotropic properties and flexibility over wide composition range
Fibres could be drawn. (First optical fibre was prepared from As_2S_3 glass)

Useful For:

- Infrared windows/ lenses/prisms, photoconductors
- Electronic switching devices, storage devices
- Acousto – optic devices for IR optical processing
- Fibres used for laser assisted surgery


10 ϕ
30
30 ϕ
80
CHALCOGENIDE GLASS
2
25 ϕ
POLISHED QUARTZ DISC
28 ϕ


Rocking furnace

BIO-GLASS/GLASS-CERAMICS

Biomaterial by definition is “ a non-drug substance suitable for inclusion in systems which augments or replaces the function of bodily tissues or organs".

Magnetic bio-glass ceramics are multiphase bioactive materials, which can generate heat (by hysteresis loss) when subjected to an externally alternating magnetic field and thus useful hyperthermia treatment of cancer

BIOMATERIALS

BIOCERAMICS

- **Bio-inert: Ceramics have no influence in surrounding living tissues**

  (Al_2O_3, ZrO_2)

  - Chosen for implants

- **Bio-active: Capable of bonding with Osseous living tissues**

  - (Ca-Phosphates, certain compositions of glass & ceramics)

Bioactivity means chemical reaction of ceramics with artificial solutions prepared to perform in vitro assays (tests)

OR

Physiological body fluids for in vivo assays

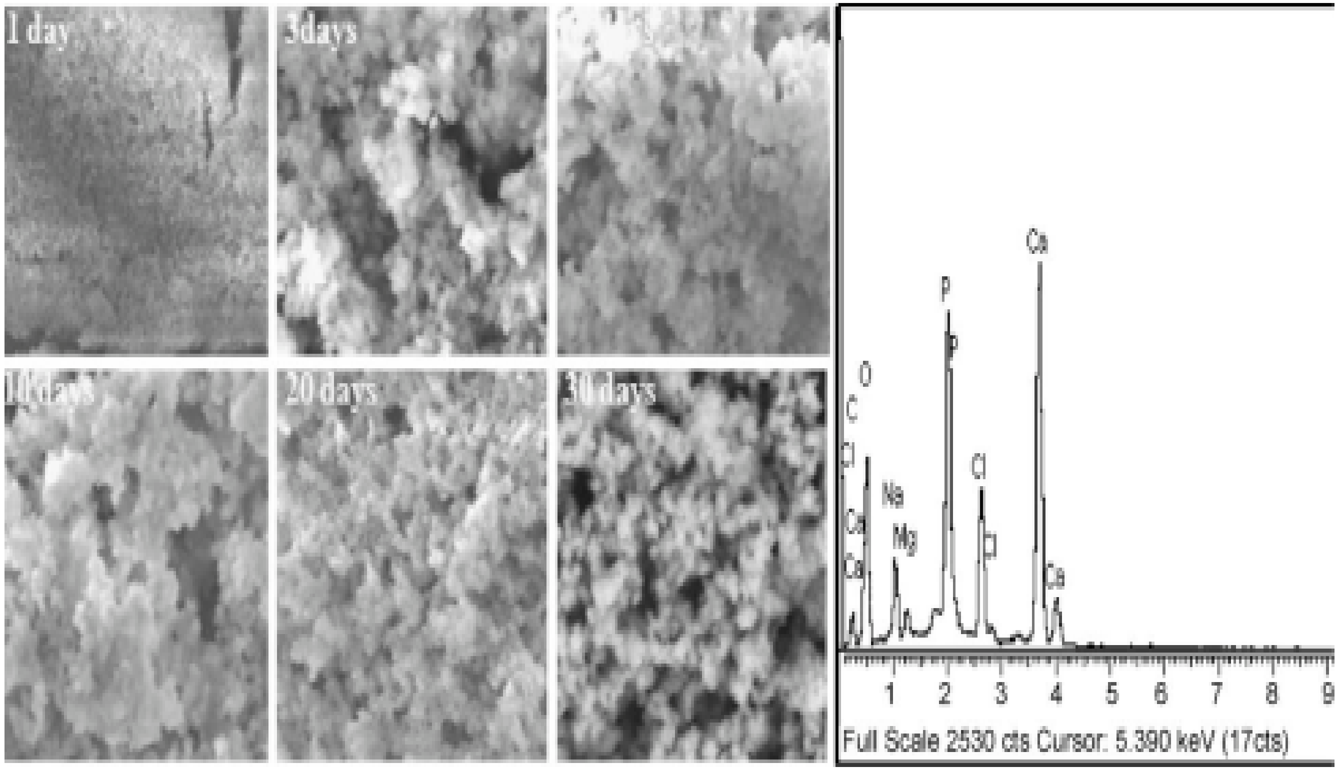
Magnetic bioactive glass/ glass-ceramics studied

- **$41CaO.(52\text{-}x)SiO_2.4P_2O_5.xFe_2O_3.3Na_2O$ ($2 \le x \le 10$ mole%) (In collaboration with IITG)**
- **$34SiO_2\text{-}(45\text{-}x)\ CaO\text{-}16P_2O_5\text{-}4.5\ MgO\text{-}0.5\ CaF_2\text{-}x\ Fe_2O_3$ (x = 10, 15, 20 wt %)**
- **$50CaO.(25)SiO_2.15P_2O_5.(10\text{-}x)Fe_2O_3.xZnO$ ($0 \le x \le 5$ mol%)**
- **$25SiO_2\text{–}(50\text{-}x)\ CaO\text{–}15P_2O_5\text{–}8Fe_2O_3\text{-}2ZnO\text{-}\ xAg$ (where x = 0, 2 & 4 mol %)**

➢ These glasses are prepared by melt quench technique,

➢ Transformed into glass-ceramics by controlled crystallization, and

➢ Characterized for magnetic and bioactive and antibactarial properties.



SEM /EDX of the glass sample with x = 8 mol.% Fe_2O_3 after immersion in SBF for 1, 3, 7, 10, 20 and 30 days, respectively. (X1000). Provide visual evidence of the formation of apatite layer. After 30 days whole surface is covered with spherical Ca–P particulate apatite layer. Ca/P molar ratio (calculated from EDS analysis) was ~of 1.67, corresponding to the value of hydroxyapatite.

Singh-Kothiyal-Srinivasan-Appl.Surf. Sci. 255(2009)6827

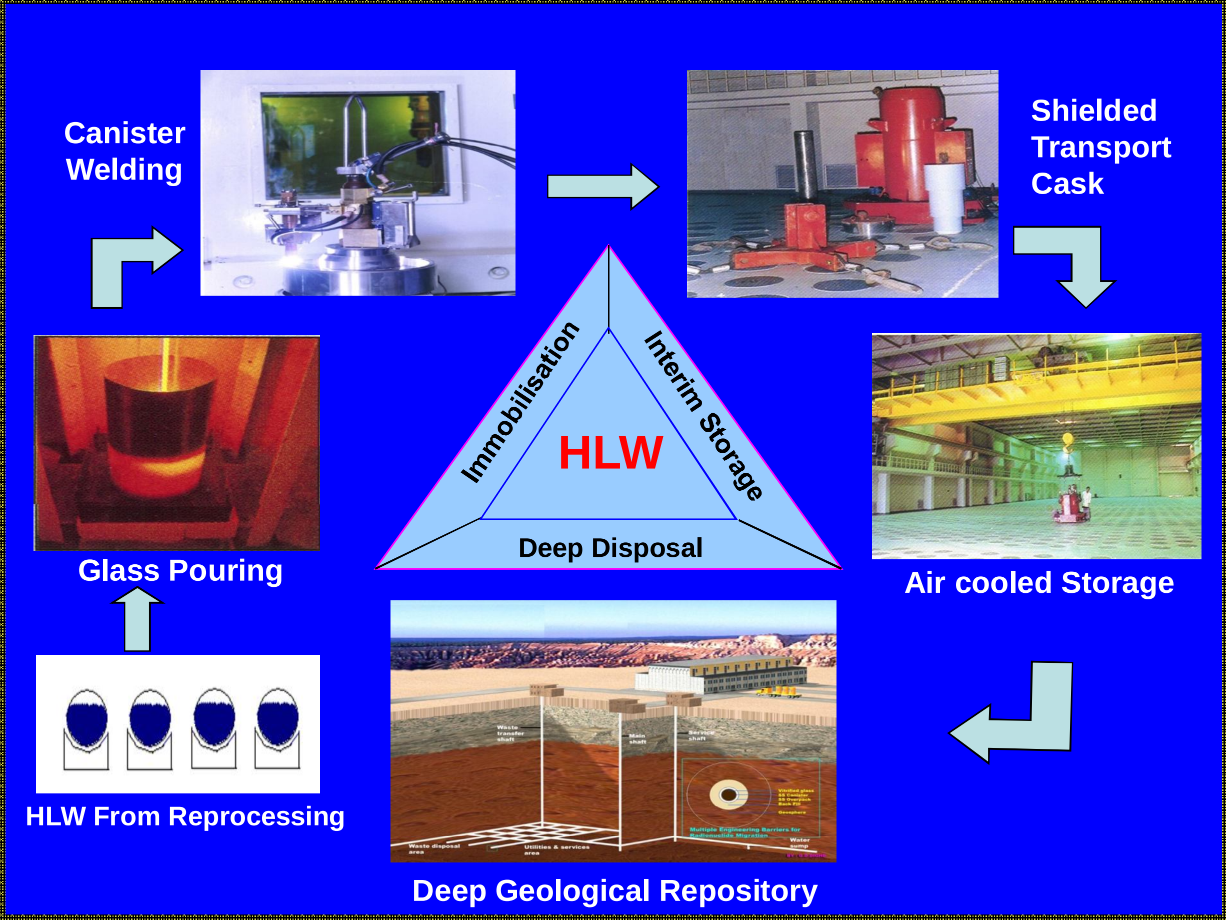
THREE STAGE STRATEGY FOR MANAGEMENT OF HLW

Dr. Homi Jahangir BHABHA

Established DAE on

August 3, 1954

1. Immobilization of waste oxides in stable and inert solid matrices.
2. Interim retrievable storage of the conditioned waste under continuous cooling.
3. Disposal in deep geological formations.



Source of High Level Waste
– Reprocessing of spent fuel

Characteristics of HLW depend on

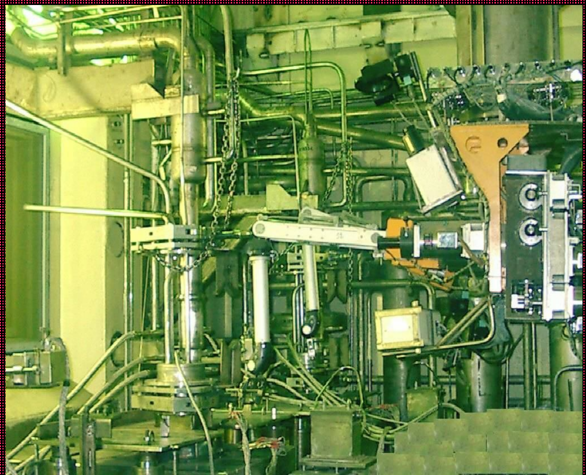
- Type of fuel and cladding material
- Burn-up and off-reactor cooling
- Decladding procedure and fuel reprocessing flow sheet

Plutonium Plant, Trombay

PREFRE - Tarapur

KARP - Kalpakkam

Indian Vitrification Facilities



WIP, Trombay

WIP, Tarapur

Advance Vitrification Facility, Tarapur

DEVELOPMENT OF GLASS MATRICES FOR VITRIFICATION

Reference glass composition was developed by BARC in collaboration with Central Glass and Ceramic Research Institute, Kolkata during 1965-1975.

TARAPUR

Waste Immobilization Plant

- **Composition modified in view of high U & Na content in waste Sodium borosilicate glass system (SiO_2-B_2O_3-Na_2O-MnO-TiO_2)**

Advance Vitrification System

- **Composition with desired resistivity to suit joule melter (SiO_2-B_2O_3-Na_2O-TiO_2-Fe_2O_3)**

TROMBAY

Waste Immobilization Plant

- **Composition to accommodate high sulphate content in waste barium borosilicate glass system. (SiO_2-B_2O_3-Na_2O-BaO)**

1. J. Mukerji and A.S.Sanyal, "Historical review: Indian Work on vitreous matrices for the containment of radioactive waste 1960-1980",Glass Technology Vol.45 No.3, June 2004.

2. C.P.Kaushik, "Development of Glass Matrices for Vitrification of Sulphate Bearing High-level Radioactive liquid Waste Generated at Trombay", Vol.5, No. 4, Oct.-Dec, 2008.

Desired Characteristics of a Matr*ix*

- Adequate leach resistance - *Isolation of radioactivity from human environment.*
- Compatibility to accept waste of varying composition.
- Homogeneous distribution of waste and glass constituents.
- Amorphous and no de-vitrification under storage condition.
- Optimum viscosity at melt temperature (1000°C) - *an important engineering parameter.*
- Low volatilization of radionuclides.
- Optimum thermal conductivity - *to facilitate dissipation of heat generated because of radioactivity.*
- Optimum electrical resistivety.
- Good thermal, mechanical and radiation stability.

Ascertaining Quality of Conditioned Product

- **Chemical durability** – an indicator of radionuclide retention – *Leaching behavior.*
- **Thermal Stability –** an index for devitrification – *Differential Thermal Analysis / Thermo-Gravimetry*
- **Homogeneity –** a measure of distribution of waste oxide & phase separation – *X ray Diffractometer / Scanning Electron Microscope / Electron Probe Micro Analyzer*
- **Radiation Stability –** an important aspect for long term durability

Development of glass frit by BARC:CGCRI

Collaborative efforts have been made by CGCRI and BARC for development and bulk production of glass frit used in Joule Heated Ceramic Melter at Advanced Vitrification System at Tarapur.

Optimization of Parameters

- Dry casting of glass with desired composition.
- Jaw crushing of glass chunk and their pulverization to obtain desired particle size.
- Nodulisation of glass powder to obtain 2-3 mm dia. beads.
- Sintering of beads to achieve desired strength.

M.S.Sonavane, "Development of Vitreous Matrices for immobilization of High-level Radioactive Liquid Waste Generated from Reprocessing of Power Reactor Fuel", Vol.5, No. 4, Oct.-Dec, 2008.

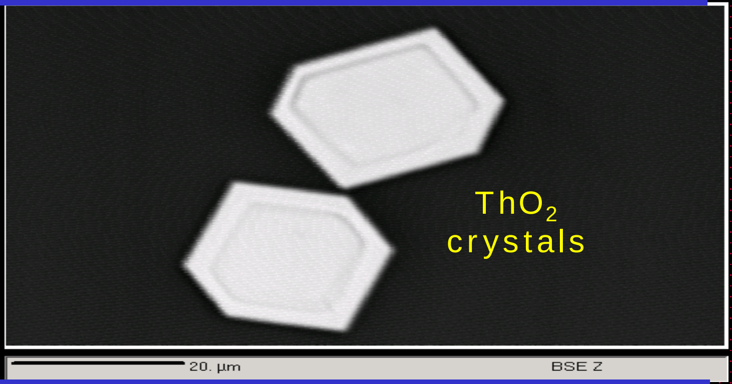
Composition of Glass Frit and Vitrified Waste Product for AVS, Tarapur

Component	Wt % for Base glass frit	Wt % for VWP
SiO_2	48.0	41.28
B_2O_3	26.5	22.79
Na_2O	11.5	9.89
TiO_2	9.5	8.17
Fe_2O_3	4.5	3.87
Waste Oxide	NIL	24.00

Development of matrices for waste generated in thoria reprocessing

- Solubility of ThO_2 in sodium borosilicate glass is limited (~5 wt %).
- Presently Barium borosilicate glass is being used for immobilization of HLW at WIP, BARC, Trombay.
- Barium borosilicate glasses developed with enhanced solubility of ThO_2 / Al / F.

BSE image showing homogeneous microstructure of BBS glass loaded with 16 wt% thoria.



BSE image showing heterogeneous microstructure of BBS glass loaded with 23.7 w% thoria.

R.K. Mishra , Pranesh Sengupta , C.P. Kaushik, A.K. Tyagi , G.B. Kale and Kanwar Raj ,"Studies on immobilization of thorium in barium borosilicate glass" J. Nucl. Mater. 360 (2007)143-150.

DESIRABLE CHARACTERISTICS OF SOLIDIFIED WASTE PRODUCT

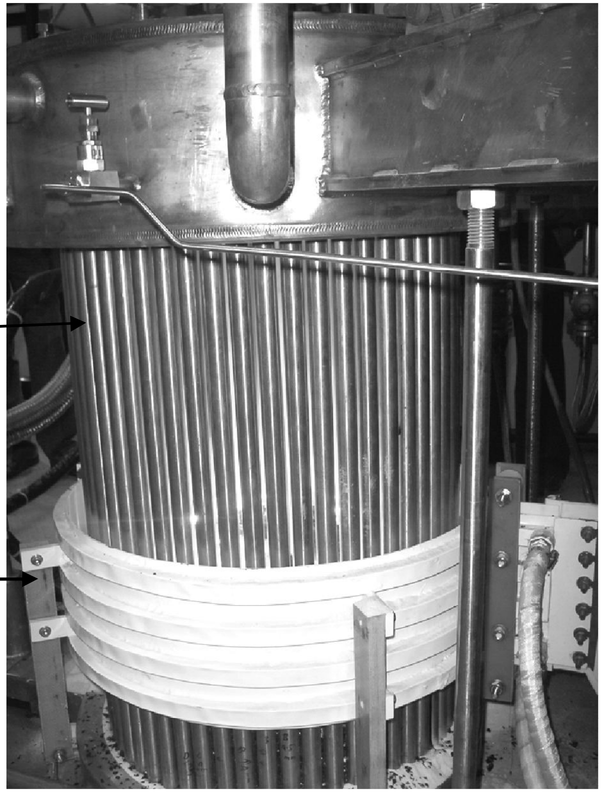
The solidified waste form must have certain properties so that its interim and long term storage followed by its ultimate disposal is technologically feasible, safe, economical and environmentally compatible. The desirable properties include:

- Good chemical durability i.e. low leachability so that activity released into the environment is minimum.
- Good thermal conductivity so that heat dissipated due to activity is not accumulated.
- Resistance to alpha, beta and gamma radiation.
- Minimum volatility of the constituents under storage conditions.
- Ability to contain high proportion of waste.
- Stability over extended period of time.
- Readily available raw materials
- Acceptable processing temperature.

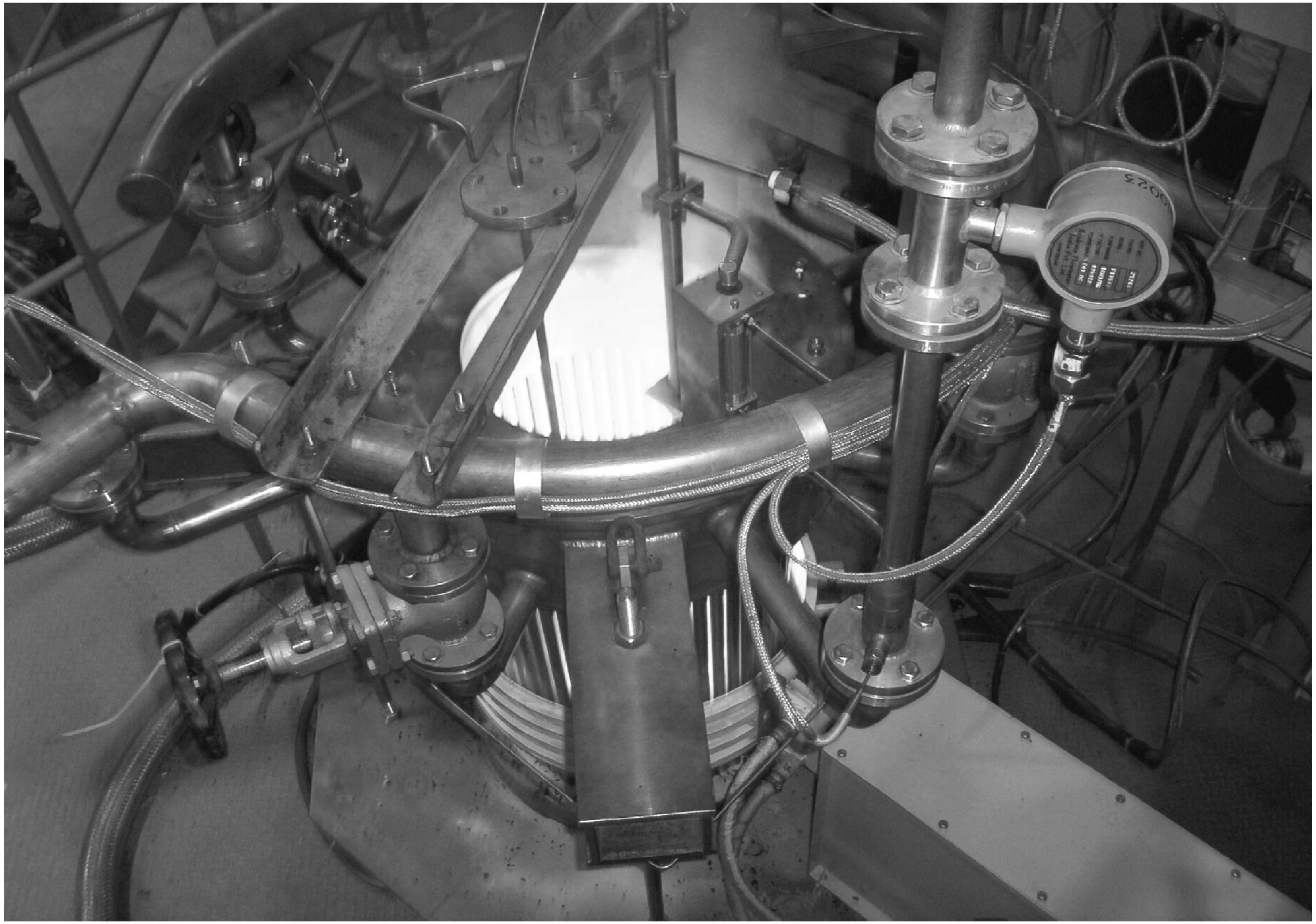
Arrangement of fingers and induction coil in cold crucible

Fingers

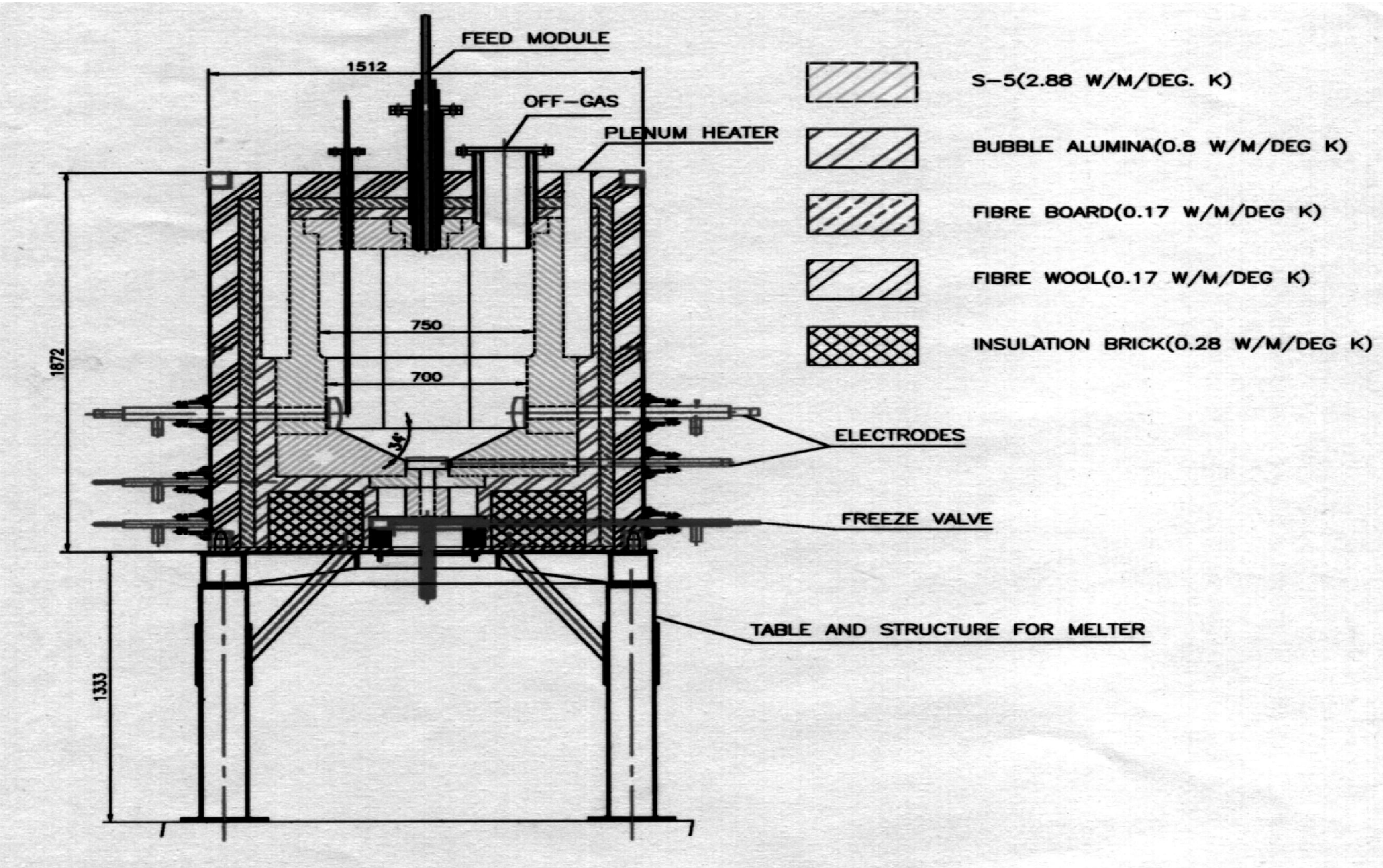
Induction coil



Melting of vitreous mass is in progress in cold crucible



Compact ceramic melter installed at AVS, Tarapur



Bulk Metallic Glasses(BMG)

- Production of BMG has opened avenues for their application in many areas where their excellent mechanical properties and corrosion resistance can be exploited.
- Transformation of amorphous phase in these alloys to one or more crystalline phases is an interesting phase transformation and can lead to formation of crystals in a variety of morphologies and a wide range of crystal sizes including nano-crystals.
- Bulk amorphous alloys exhibit higher fracture stress combined with higher hardness and lower young's modulus than those of any crystalline alloy.
- Bulk amorphous alloys have high bending and flexural strength values that are 2. 0 to 2.5 times higher than those for crystalline Zr- and Ti-based alloys. The composites of bulk metallic glasses containing crystalline phases have been found to have special properties.
- This has been demonstrated in case of composites of bulk metallic glass and tungsten wires with the glass forming the matrix. Such a composite displays high impact strength and is especially suitable for application as an armour penetrator in various types of armour piercing shells used in the defence industry.

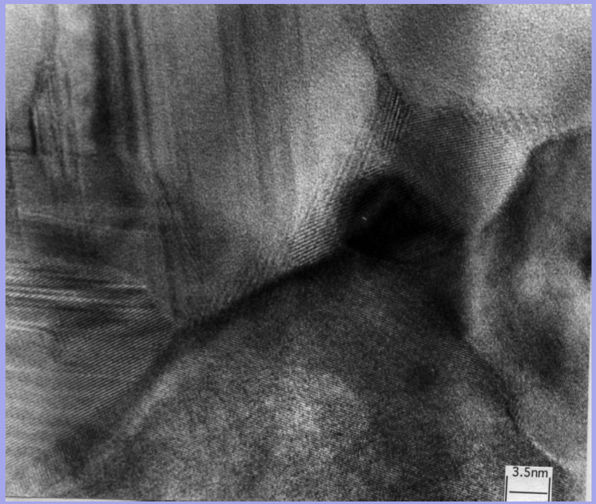
- BMG have already found application in form of sporting goods. Since the elastic strain shown by BMG is about twice that of the best crystalline spring material, the energy stored in elastic region of metallic glass is about four times greater. This property has been used in a variety of sporting goods such as golf clubs, base ball bats and sporting cycle spokes.

Zr-based Metallic Glass: $Zr_{52}Ti_6Al_{10}Cu_{18}Ni_{14}$

- $Zr_{52}Ti_6Al_{10}Cu_{18}Ni_{14}$ **crystallized at 923 K for 2 hours showing nanogains in the size range of 10 – 50 nm.**

- **HREM image of a nanograin boundary in the crystallized bulk metallic glass shows the lattice fringes in the nanograins : travelling from one end of the nanograin to the other and extended almost up to the nanograin boundary.**

a)



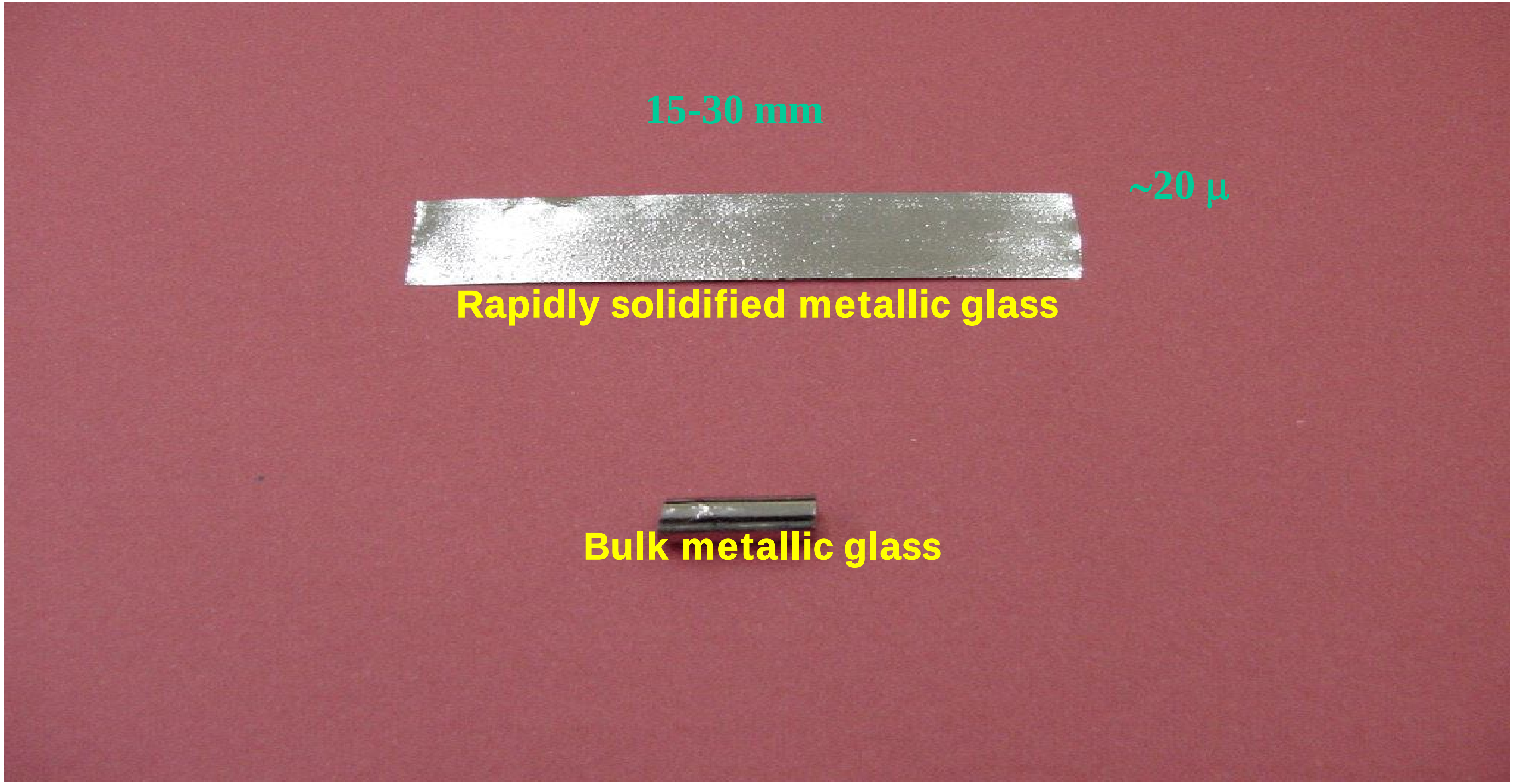
b)

a) Conventional TEM-Nanocrystallized microstructure in alloy

b) HREM of nanocrystallized microstructure.

Melt Spinning

Typical Appearance



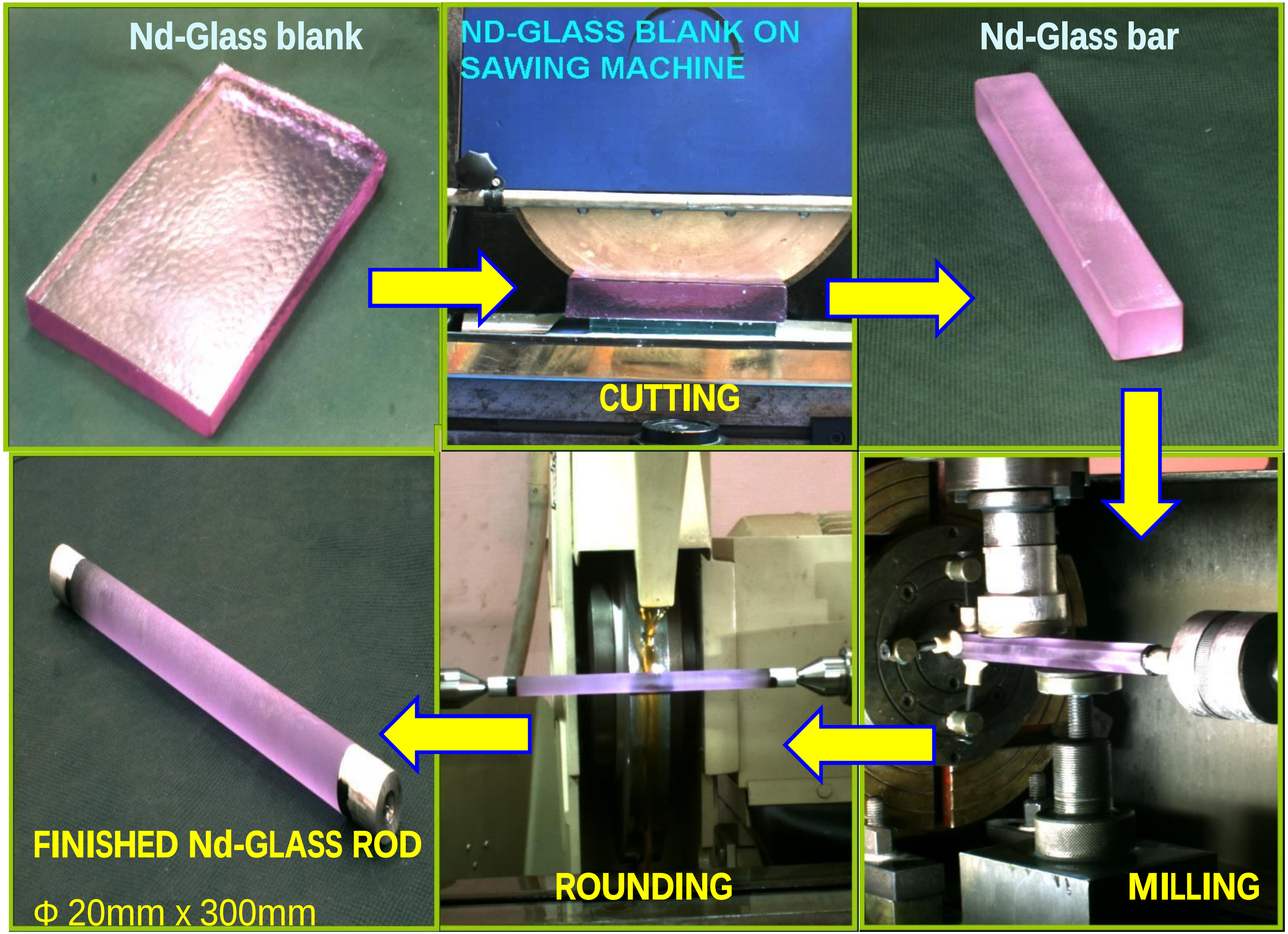
Some Efforts to Develop Laser Glass-

(Joint Efforts by CGCRI, BARC, RRCAT)

A program to indigenously develop Nd doped phosphate laser glass equivalent to LHG-8 of M/s Hoya Ltd. was funded by Board for Research in Nuclear Sciences (BRNS) under memorandum of understanding (MOU) with participation of Central Glass and Ceramic Research Institute (CGCRI), Bhabha Atomic Research Centre (BARC) and Raja Ramanna Centre for Advanced Technology (RRCAT) to develop good quality laser glass rods and discs for High Energy, High Power (HEHP) Lasers.

S No	Glass Block Size L x B x H (mm)	Nd_2O_3 doping wt%
1	12X12X170	3.0
2	17X17X210	2.5
3	28X28X320	1.5
4	54x54x320	1.0
5	69X69X320	0.8
6	85X170X20 (Disc)	2.2
8	105X210X20(Disc)	2.2

Fabrication of Nd:glass rods in RRCAT



Comparison of Important properties of the CGCRI Laser glass & LHG-8 after stage-I

Properties	Values for Hoya glass (LHG-8)	Values for our glass (INLG 27)
Physical and Optical Properties		
Nd^2O^3 concentration (Wt%)	3.03	3.00
Nd^{3+} concentration (x 10^{20} ions/cm^3)	3.074	3.026
Density ($g.cm^{-3}$)	2.78	2.8179
Refractive index, n^e	1.529	1.5301
Abbe number (νd)*	66.5	66.13
Non-linear refractive index coefficient γ (x10^{-20} m^2/W)	3.08	3.02
Stimulated emission cross section (10^{-20} cm^2)	3.36	2.7
Thermal Properties		
Glass transition temp. (^{0}C)	487	502.8
Sag temperature (^{0}C)	524	538.3
Coefficient of linear thermal expansion ($10^{-7}/^0$C) (20-1200C), α^{20-120}	107	110
Spectroscopic Properties		
Fluorescence Peak (nm)	1053	1053
Fluorescence half line width (nm)	27	26.5
Fluorescence Lifetime (μs)	350	310
Attenuation coefficient at 1053 nm (cm^{-1})	0.001	0.0018
Absorption Coefficient at 3000 cm^{-1} (α^{OH-1})	3.0	3.86

Radiation resistant optical fiber

- Refers to the resistance of an optical fiber to change its optical transmission due to exposure to x-rays, γ-rays, α, β particles, neutrons
- Defect centers formed due to absorption of these radiations cause attenuation of transmission
- Extent of damage/attenuation depends upon
  - amount and type of dopants/impurities in the fiber
  - temperature of the fiber during and after exposure
  - type of radiation incident upon the fiber
  - radiation dose rate and total dose
  - number of separate exposures experienced by the fiber

Radiation resistant optical fiber

Radiation resistant optical fiber finds a wide range of applications in nuclear establishment

- Optical signal transmission instead of conventional electrical signal transmission in radioactive environment (e.g., Fusion reactor).
- Optical imaging inside reactor for quality control
- Data collection in radioactive environment and processing in inactive area
- Measurement of Physical and Chemical parameters for process control

On the contrary radiation induced absorption is important for applications in

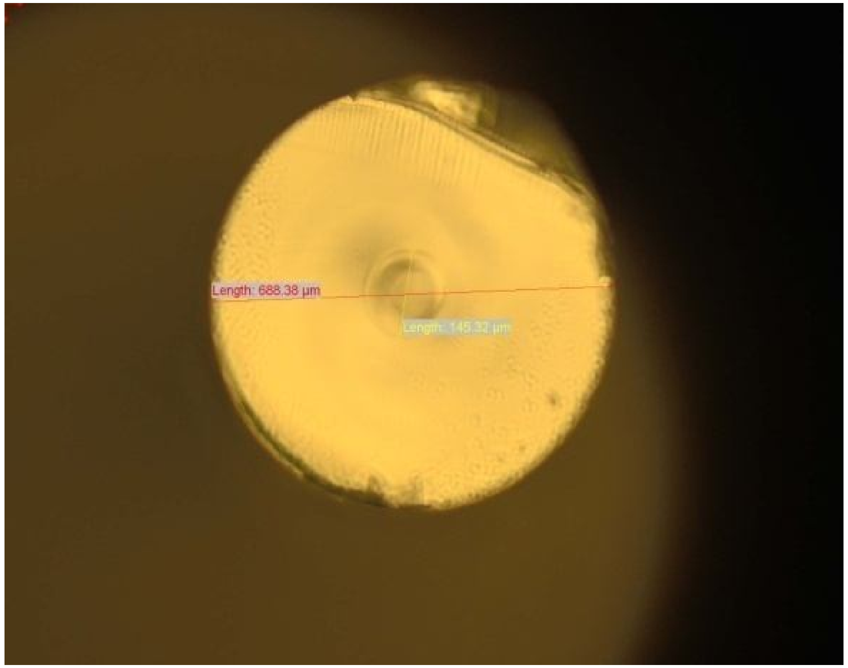
- ***Fiber Dosimeter***

Fiber lasers, sensors , and fiberscopes are also of interest to nuclear industry.

Joint project by CGCRI & BARC - develop pure silica core step index multimode optical fiber with F doped silica cladding to transmit UV & VIS light for fluorescence measurement in radioactive environment as pure silica resists radiation damage. Studies involve

- Preparation of core and cladding preforms of a given design and composition by MCVD process
- Drawing of fibers from the preforms and characterization of geometrical & optical properties.
- Testing the radiation response behavior under cumulated dose of 1MRad γ-radiation
- FTIR investigation of the defect and structural changes in the core glass.

Specs of fiber developed. Core: Pure silica, Clad: F-doped silica, OH concentration: <5 ppm



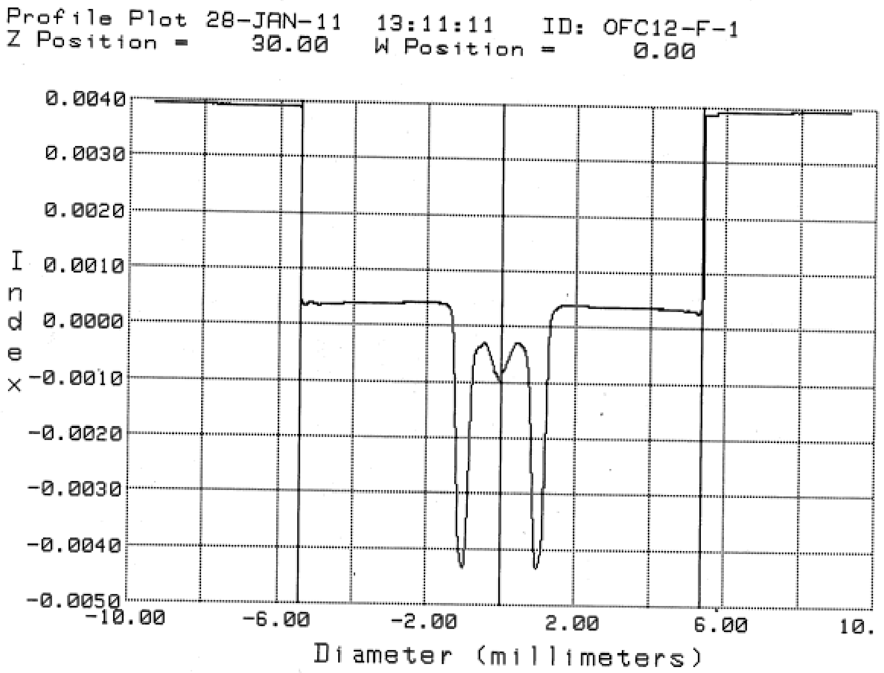
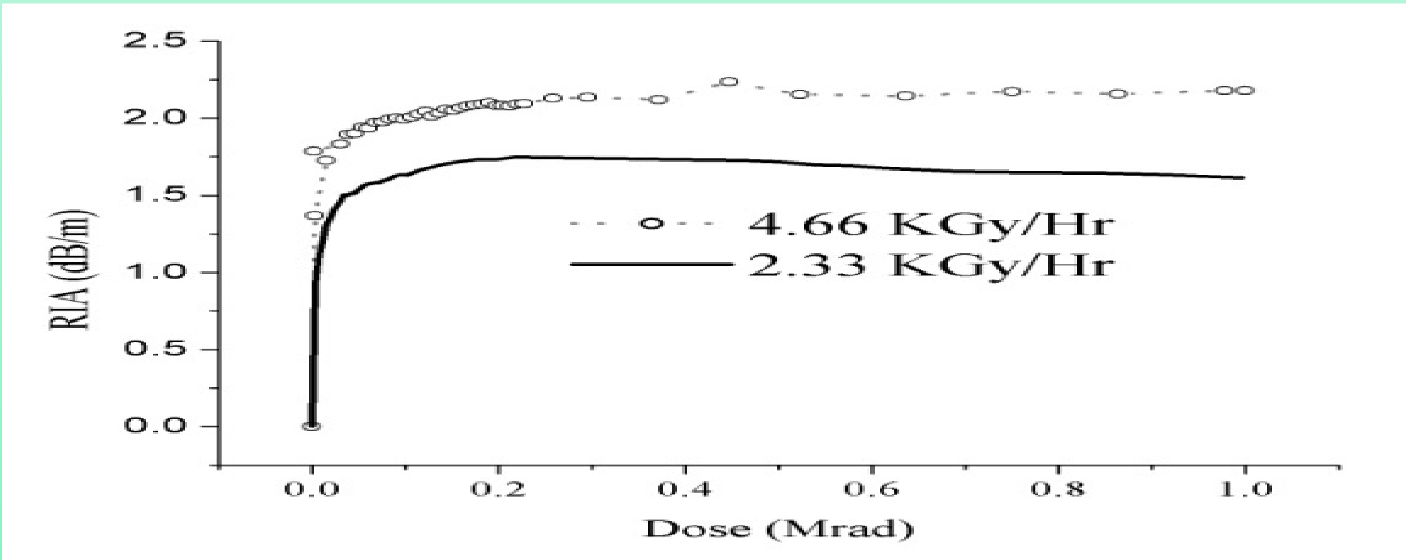


Fig: 1 Cross-sectional view of a pure silica core fluorine down-doped preform produced at CGCRI.

Fig: 2 Refractive index profile of a pure silica core fluorine down-doped preform produced at CGCRI.

Results:

Radiation Induced Attenuation in the wavelength range of 200 to 850 nm under γ irradiation with dose rates of 4.66 kGy/hr and 2.33 kGy/hr for a cumulative dose of 1MRad studied for this fiber and compared with fibers having higher OH concentration and chlorine impurity.

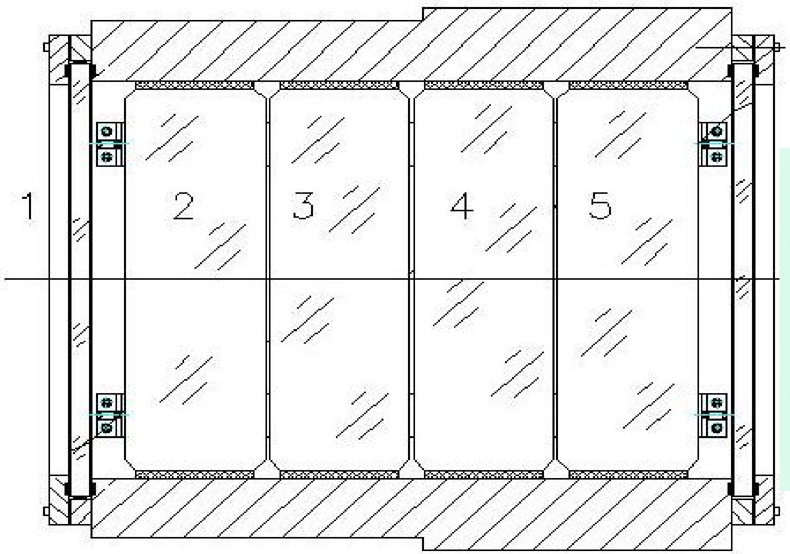


❖Conclusions:

1. Two absorption peaks at 450 and 630 nm appear due to defect in silica.
2. Fibers with high OH content provide better radiation resistance property in the near visible region (400-500 nm) although there is a significant absorption peak at 630 nm.
3. Fibers with low OH content show higher RIA in the range of 400-500 nm due to broad UV absorption band and in absence of Cl_2 show no peak at 630 nm.
4. It is important to identify suitable fiber compositions for discrete wavelength zones in the visible range (i.e 400-500 nm and 600-700 nm) for achieving maximum radiation tolerance instead of a single composition for the entire visible wavelength zone.

Indigenization of Manufacturing Technology for Radiation Shielding Glasses

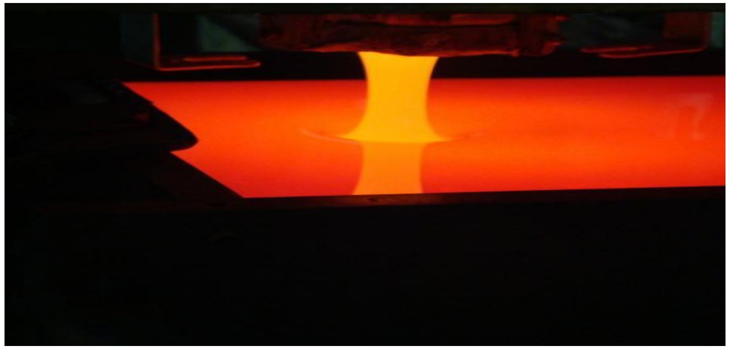
Radiation Shielding Windows (RSWs) are made up of special glasses with good internal transmission, low reflection value, high refractive index and high radiation stability.



Typical RSW construction

1 & 2 : Low density glass (2.52 g/cc) (Ceria stabilized)
3 & 4 : Medium density glass (3.6 g/cc)
5 : High density glass (5.2 g/cc)
6 : Borosilicate glass of 2.52 gm/cc)

RSW Glass Manufacturing Facility at CGCRI



Facility for RSW glasses (400x400x100mm, high density)

Thank you All

for your kind attention !!!!

Thank you All

for your kind attention !!!!

*Some Colleagues and Collaborator**


50
BARC

Bhabha Atomic Research Centre

Metal-non metal bonding theories

•Thermo-dynamical approach - when a liquid is brought into contact with solid, a new interface is created between the liquid and solid, liquid will spread only if the resultant energy of new solid – liquid interface is less than that of the corresponding solid –vapour interface

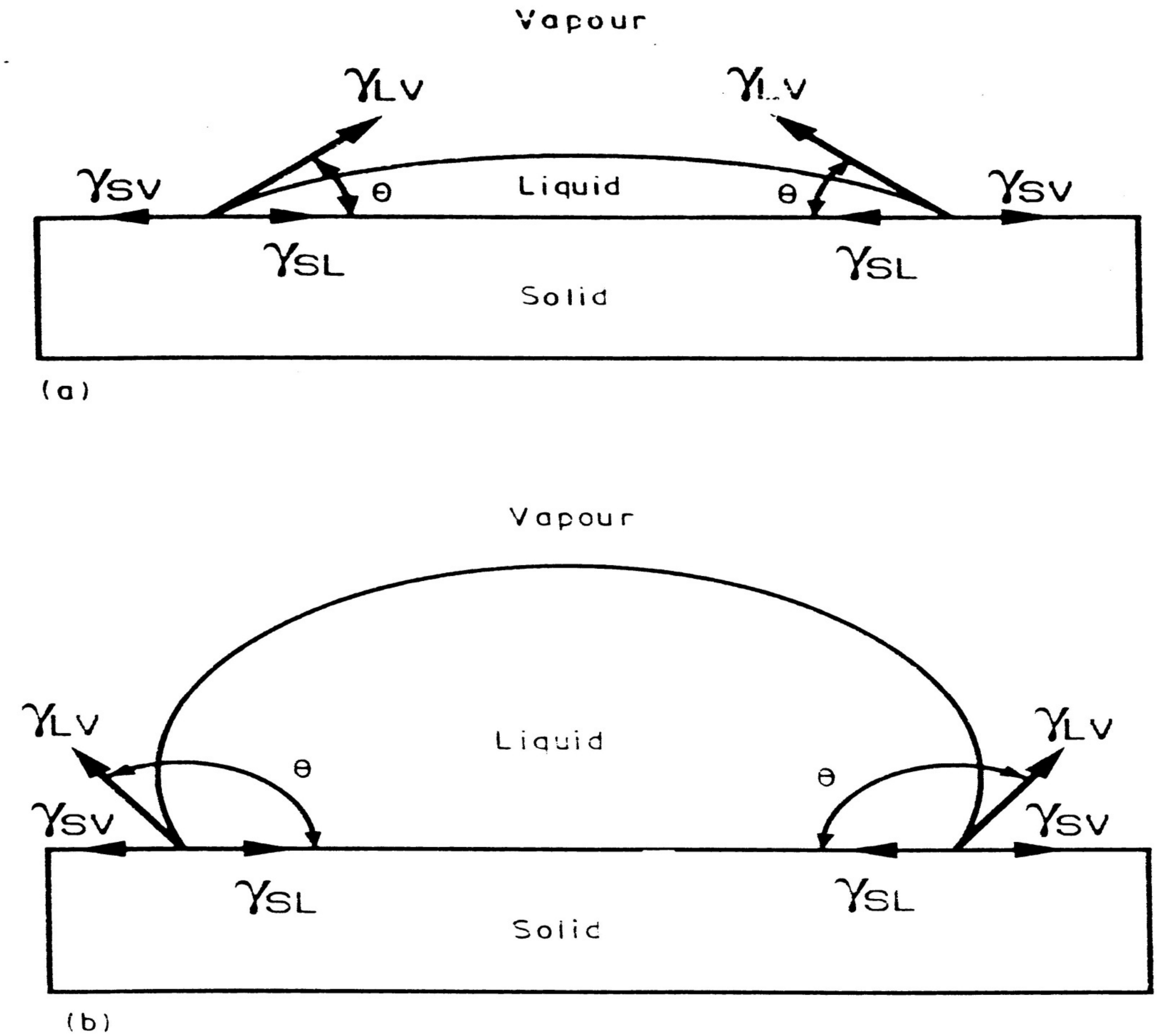
•Greater the difference, greater the spreading/wetting **(Driving force for wetting is related to the difference in energy between solid-vapour and solid-liquid interfaces)**

Assumption: No reaction between liquid & solid, **But Chemical reaction may give new compound and hence wetting and adhesion-oxidation of metal surface enhances adhesion**

•Lowest surface energy configuration of for a liquid is a sphere,

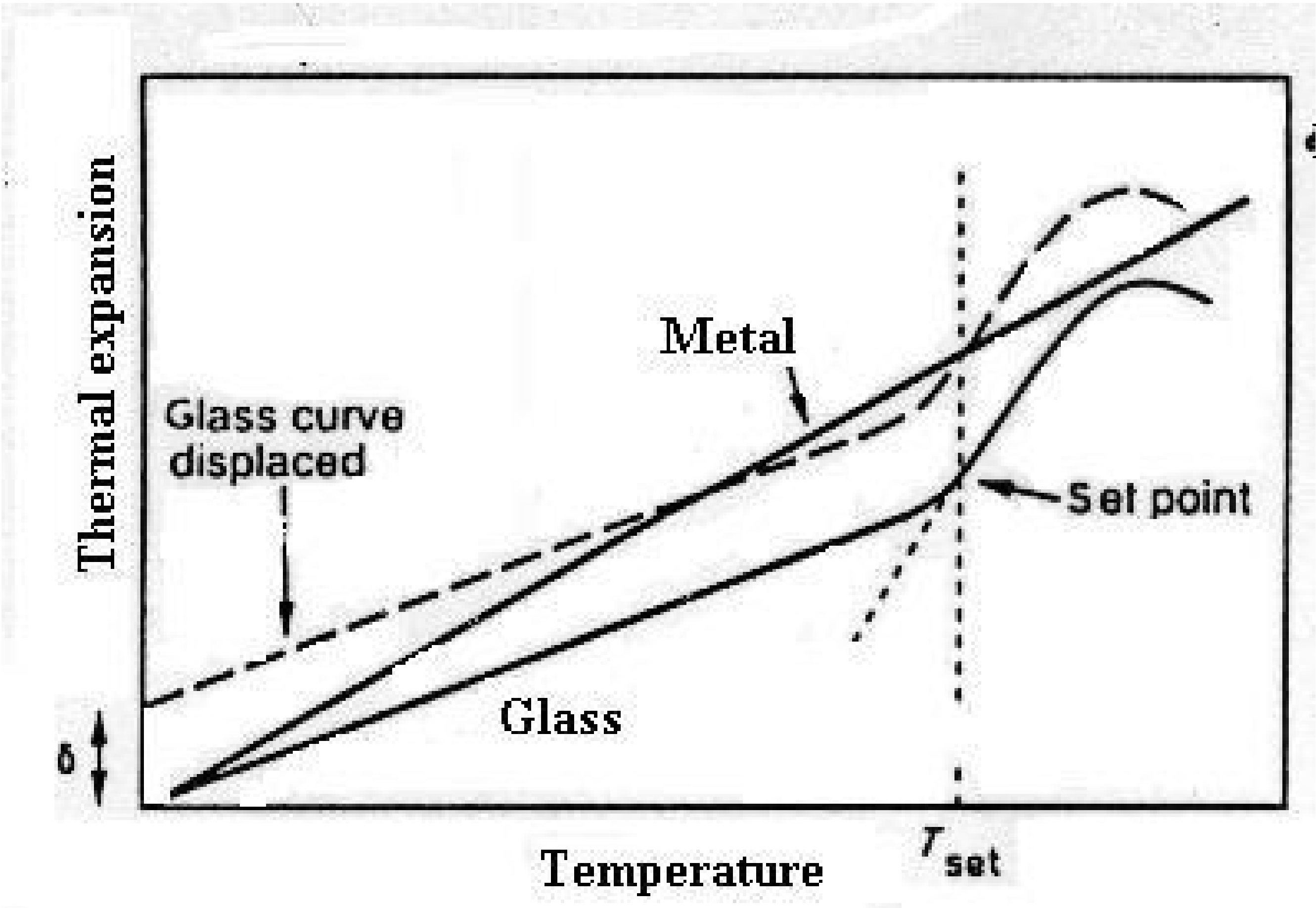
hence the role of contact angle θ is important. Wets when $\theta < 90^{o}$

•$\gamma_{SV} = \gamma_{SL} + \gamma_{LV} \cos\theta$



Sessile drop configuration (a) wetting, (b) non-wetting

Thermal expansion curve for a metal and glass



- For a good seal

$\delta < 4 \times 10^{-4}$

Glass and Advanced Ceramics Division
(G&ACD)

MATERIALS RESEARCH

Major activities

- ❖ **Glasses (Oxides) : Sealants**
- ▪ **Lead silicate, borosilicate, phosphate glasses, lead free oxides etc.**
- ❖ **Glass (Non Oxides) : Optical Application**
- ▪ **(Arsenic & Antimony chalcogenides/ chalcohalide).**

❖**Glass-ceramics(GCs)**

- **Machinable GC : Magnesium-Aluminium-Silicate (MAS)**
- **Sealants : Ambient : Lithium-Zinc-Silicate (LZS),**
  Lithium Aluminum Silicate LAS),
  High temperature : Barium /Strontium Zinc Silicate (B/SZS),
  Ba-Ca-Al-B-Silicate (BCABS)

Bio-compatible GCs: Iron/Zn doped phosphate-silicate & boro- phosphate,

---

Advanced Ceramics: SiC, Lanthanum Strontium Magnetite, Piezoelectric ceramics Pb- La- (Zr Ti) O_3 (PLZT) , Yttrium doped barium zirconate (BZY)

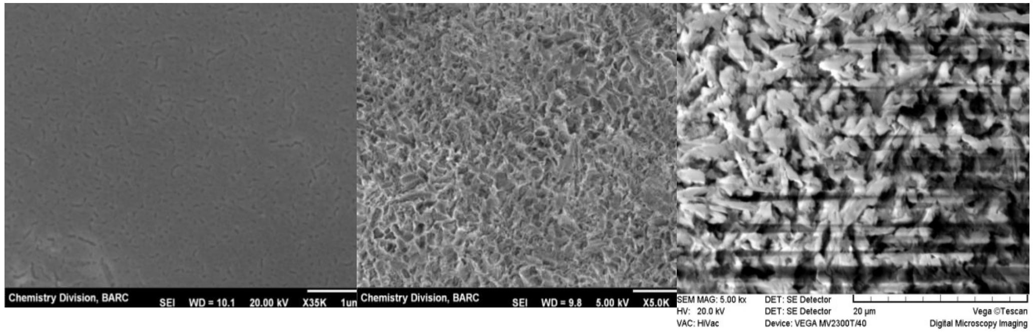
Plan of talk

- General introduction
- What are Glass/ glass-ceramics?
- Functionalities in Glass/ glass-ceramics
- Different systems investigated
- Summary/Conclusion

Crystallization Studies of SZS glass

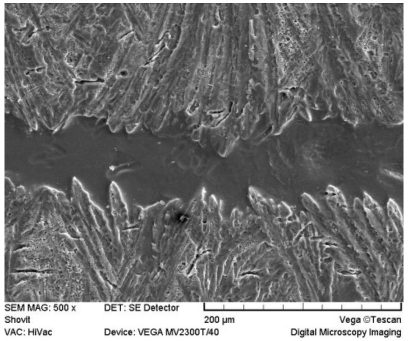
Crystallization kinetics was studied using Kisssinger method and Matusita and Sakka method (modified form of Kisssinger model). Phase evaluation was studied by SEM and XRD.

SZS-1 glass

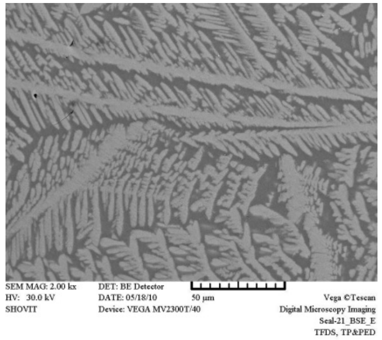


750 C/5 h　　820 C/2h　　925 C/2 h

SZS-6 glass



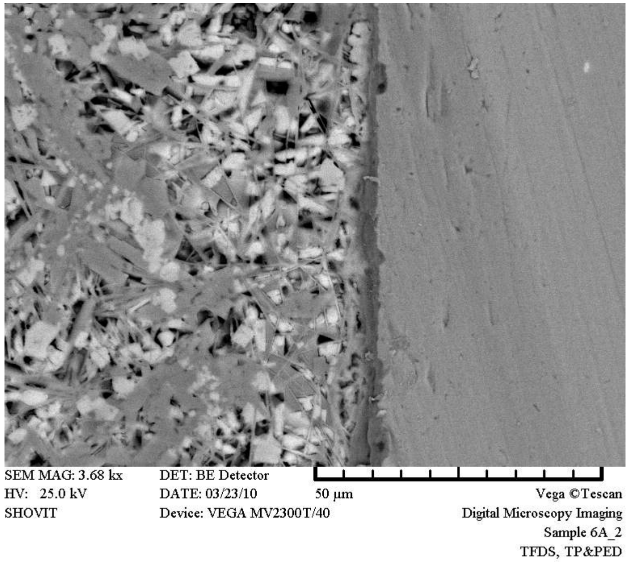
SZS-8 glass



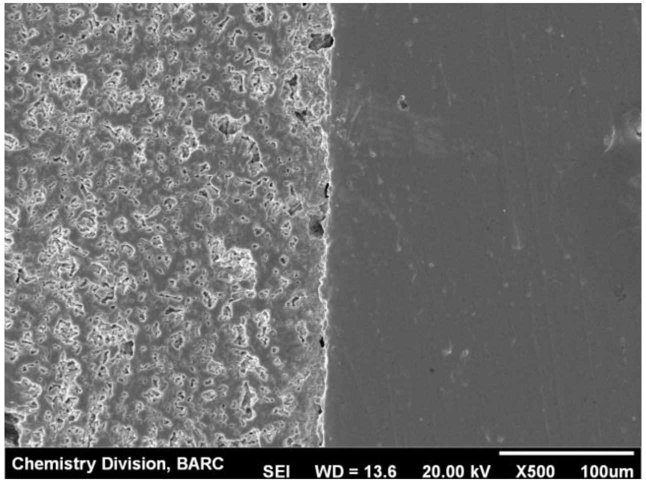
Evaluation of microstructure of SZS-1 glass with temperature revealed that this glass crystallize by liquid-liquid phase separation by spinodal decomposition mechanism and resulted in highly interconnected microstructure of 2 phases.

Bulk crystallization occur in SZS-1 glass and with the addition of B2O3 tendency toward Surface crystallization increases.
Surface crystallization is more dominant in SZS-6 glass
Bulk crystallization is dominant over surface crystallization in SZS-9 glass

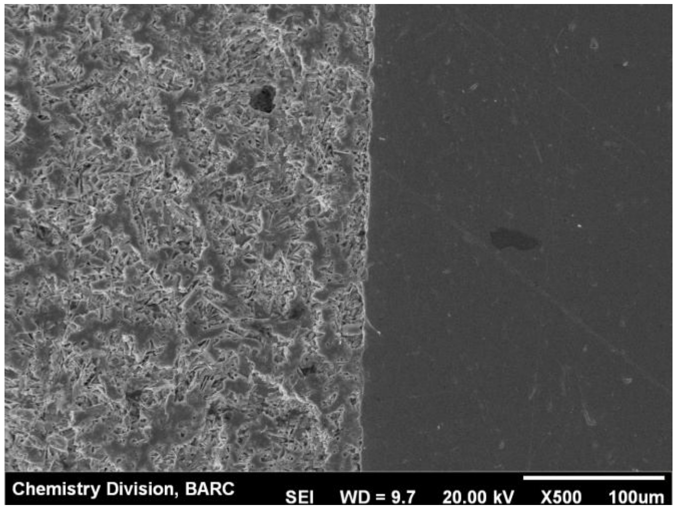
Microstructures at the interface of the BCABS glasses with Crofer 22 seals after heat treatment of 300hrs at 775°C



BCABS-TiO_2



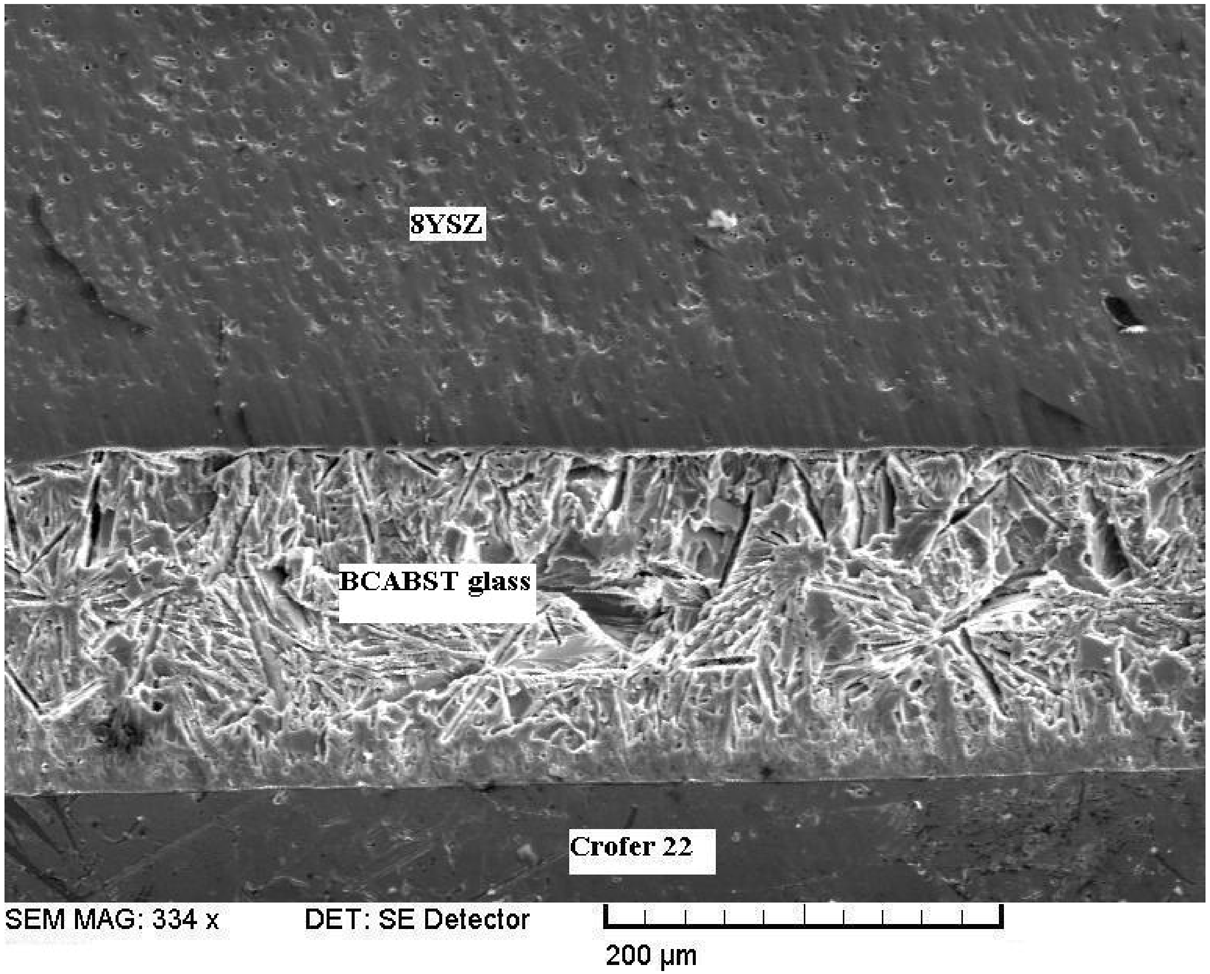
BCABS-Cr_2O3



(BCABS-P_2O_5

Continuous crack free interface indicates Good bonding

Microstructure near the interfaces of 8YSZ/BCABST glass/Crofer 22 alloy.



SZS glasses

Strontium zinc silicate glasses with different additives like B_2O_3, Al_2O_3, V_2O_5, Cr_2O_3 etc. were prepared by melt-quench method and transformed into glass-ceramics by controlled crystallization

Prepared compositions (in wt%)

Glass ID	SrO	ZnO	SiO_2	B_2O_3	P_2O_5	Al_2O_3	V_2O_5	Cr_2O_3	TiO_2	Y_2O_3
SZS-1	51	9	40	-	-	-	-	-	-	-
SZS-2	51	9	35	-	-	3	-	2	-	-
SZS-3	51	9	30	5	-	3	-	2	-	-
SZS-4	51	9	30	10	-	-	-	-	-	-
SZS-5	51	9	30	-	10	-	-	-	-	-
SZS-6	49.1	8.9	29.2	8.5	-	-	4.4	-	-	-
SZS-7	49.4	9	29.4	8.5	-	-	-	3.7	-	-
SZS-8	48.8	8.8	27.6	6.7	-	2.5	-	3.7	1.9	-
SZS-9	48.1	9.4	27.9	1.6	-	2.4	-	3.5	1.9	5.2

Glasses and glass-ceramics have desired TEC (90-110 x $10^{-7}/^{o}C$) and sufficiently high T_{ds} as required for SOFC sealant. Glass-ceramics comprise of $Sr_2ZnSi_2O_7$ and $SrSiO_3$ crystalline phases.

Babita…Kothiyal, J Hyd. Energy, (2011)

Indigenized Production of RSW Glasses

•***Bharat Ophthalmic Glass Ltd., Durgapur and***

•***Central Glass & Ceramic Research Institute, Kolkata were identified for indigenous production.***

BOGL produced low and medium density RSW glasses

High density glasses was produced in a mutual collaborative work between BARC and CGCRI with the success of the initial lab scale translating into a full plant-scale facility through MoU route.

• ***264 Glass blocks (150x150x100 mm) were supplied by CGCRI under this MOU by 2006.***

CONCLUSIONS-1

- We have studied various glass-Ceramics having Applications as sealants materials
- Electron Microscopy has helped us in understanding mechanism of bonding of glass-ceramics-to-metal as well as influence of metal on the microstructure
- High temperature XRD and MAS NMR brought out the useful information on phase formation and bonding structure

Future requirements of RSW Glasses

Confidence acquired by CGCRI team resulted in trial production of 550x550x50 mm glass blocks by slumping technology. This could meet DAE's urgent requirements.

Further development will include production of Large size glass blocks (700x700x100 mm)

Development of alternate crucible (Clay crucible *to replace* ***Platinum) will can lead to better cost effectiveness.***

About 150 Tones of RSW of varying density will be required for the upcoming plants in the back end fuel cycle.