MATERIALS RESEARCH IN BHABHA ATOMIC RESEARCH CENTRE

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Areas of Materials Research

1. Nuclear Fuels
2. Structural Materials for Nuclear Reactors
3. Neutron Scattering for Materials Characterization
4. Glass & Ceramics
5. Magnetic & Spintronic Materials
6. Electronic Materials
7. Energy Conversion Materials
8. Superconducting Materials
Three Stage Indian Nuclear Power Programme

1. To maximize the energy potential from domestic Uranium and Thorium resources.
2. Energy security and demonstrate sustainability of nuclear power.
3. Minimize Green House Gas emissions while meeting the huge demand for electricity.

Closed fuel cycle is the integral part of this strategy.
Three Stage Indian Nuclear Power Programme - Strategy

Stage 1
- Power generation primarily by PHWR
- Building fissile inventory for stage 2

Stage 2
- Expanding power programme
- Building U$^{233}$ inventory

Stage 3
- Thorium utilization for Sustainable power programme

U$^{233}$ Fueled Breeders
Pu Fueled Fast Breeders

PHWR
FBTR
AHWR

Nat. U → U fueled PHWRs → Electricity
Dep. U
Pu

300 GWe-Year
42000 GWe-Year
155000 GWe-Year
Pushing the burn-up

- For better nuclear fuel utilisation
- To extend re-load intervals
- Lower fuel cycle cost

Fuel
- Fuel restructuring
- Fission gas release
- Fuel clad interactions
- Reactivity Control
- Safety Behavior

Structural materials
- Radiation damage
  - Dimensional stability
  - Property degradation
- Clad - coolant compatibility
Mixed Oxide (MOX) Fuels for Pressurized Heavy Water Reactors (PHWRs)

Development of high burn-up fuels for use in PHWRs

- 50 MOX fuel bundles fabricated at BARC.
- All the MOX bundles are irradiated in KAPS-1 and peak burn up achieved is 20,000Mwd/t.
- **Demonstration of capability** to manufacture & utilize MOX fuels for PHWRs

Fuel subassembly inside glove box

End plate welding of PHWR MOX bundle at AFFF
• Kamini is a Neutron Source Reactor fuelled by $^{233}U$ based $UA_3$ dispersion fuel.
• Ingot metallurgy & powder metallurgy routes developed.
• Hot rolling, swaging & picture framing technique.
Development efforts for high density uranium compounds/alloys

- Development of $\text{U}_3\text{Si}_2$ compound by an innovative powder metallurgy route for modified APSARA core.

- Development of U-Mo alloys for dispersion fuel application for advanced research reactors
Fabrication of Mixed Carbide Fuel for Fast Breeder Test Reactor (FBTR) at Kalpakkam

- $(U_{0.3}Pu_{0.7})$ Mixed Carbide (MK I) and $(U_{0.45}Pu_{0.55})$ Mixed Carbide fuel (MK II) was chosen as fuel for FBTR at Kalpakkam.
- High thermal conductivity and metal density in MC lead to compact core & high breeding ratio.
- Performance of this fuel has been proved to be excellent and is at present beyond 150,000 MWD/T.
- Technology is highly complex but can be adopted for small cores.
Development of shorter doubling time fast reactor fuel

- Glove box set-up for injection casting & swaging and testing of U fuel slugs fully installed.
- Cold commissioning trials with U-5%Zr rods.
- Optimization of parameters.
Fuel fabrication for Prototype-FBR

• Fabrication Technology for MOX Fuel Established
• Experimental irradiation of PFBR MOX fuel (with U-233) in FBTR: fuel has reached 60 GWd/t burn-up
• Fuel specifications optimised for product recovery as well as performance
• R&D on metallic fuel for achieving shorter doubling time
Carbide fuel for Fast Breeder Test Reactor

- Comprehensive Post Irradiation Examination of FBTR fuel at 25, 50 and 100 GWd/t in hot cells under inert atmosphere:

- Destructive as well as non-destructive techniques employed

- FBTR Mark I Fuel has now reached 155 GWd/t without fuel pin failure in the core

- Fuel discharged at 25, 50 and 100 GWd/t reprocessed in CORAL facility
Fuel for Compact High Temperature Reactor

Coated fuel particle Ø900micron

Graphite Fuel Tube

Fuel compact Ø10mm, 35mm long

Outer Steel Shell
Gas Gaps
High Conductivity shells
Inner Shell
Graphite Reflector
Downcomer Tubes
BeO Reflector
Reactor Regulating System
BeO Moderator
Fuel Tube
Fuel

CHTR Reactor core
Structural Materials Research

(For Thermal Reactors)

1. Zirconium alloys for cladding, pressure tubes for thermal reactors

(for High Temp. Reactors)

1. Refractory metal alloys
2. Beryllium and its alloys
3. Carbon based materials

(for Fast Reactors)

1. Ni based alloys
2. Oxide dispersed stainless steel
Comprehensive Condensed Matter Research Programme

- Neutron
- Electron
- X-ray Synchrotron

- High Pressure
- High Strain rate
- High magnetic field
- Low and high Temperature

Basic & Applied Research

Structure, Dynamics, Magnetism, Electrical & Thermal Transport, Optics, etc.

Bulk, Nano, Amorphous...
Capabilities of National Facility for Neutron Beam Research

**Diffraction (structure)**
- Wide-angle scattering (crystals, strain distribution)
- Very-large angle scattering (glasses, liquids)
- Small-angle scattering (large molecules, thin films)
- Neutron polarization analysis (magnetic systems)

**Spectroscopy (Dynamics)**
- Inelastic and quasi-elastic scattering
- Neutron Imaging/Tomography/Radiography
- Neutron Optics / Fundamental Physics

Another emphasis will be on R&D on Magnetic Materials for Energy Systems such as molecular magnets and high magnetocaloric materials.
Studies using Neutrons

Structure
- Wide angle diffraction (crystallography, magnetism, strain distribution)
- Very large angle diffraction (glasses, liquids)
- Polarized neutron scattering (magnetism)
- Small angle scattering (large molecules, thin films)

Dynamics
- Inelastic scattering (deterministic) and
- Quasi-elastic scattering (stochastic)

Fundamental Quantum Physics - Neutron Optics
Neutron Imaging - Tomography/Radiography
Carbon Based Materials

- Pyrolytic carbon
- Carbon Nanotubes and Nanofibres
- Carbon coated fuels
- Metal carbides like SiC
- Diamond and diamond-like carbon films
- Boron carbide for nuclear applications
- Carbon based composites
Research on Glasses

- Glasses for nuclear waste immobilization
- Glass sealants for Solid Oxide Fuel Cells
- Radiation stable glasses
- Laser Glasses
- Machinable glasses
- Glass to ceramic / metal seals
- Glass-ceramics
Development of Borosilicate glasses for Nuclear Waste Immobilization

Higher waste loading, Thermal and Radiation stability, Low leaching rates

**Phase I**

**Immobilization in inert solid matrix, viz., glass**

Metallic melter, WIP Trombay

Ceramic melter, AVS Tarapur

Cold crucible, Demo facility

**Phase II**

Interim storage of vitrified waste for 25-30 years

Solid Storage & Surveillance Facility

Canister & overpack

Overpack placement cask

**Phase III**

Final disposal in deep geological repository

Multiple barrier

- Canister cap
- Canister
- Overpack
- Backfill
- Geological media (granitic host rock)

Underground Repository Lab

Conceptual geological repository
Materials for Energy Conversion

- Electrolytes, Cathode, Anode and Interconnect materials for Solid Oxide Fuel Cells
- Materials for H₂ production (Thermochemical and photochemical routes)
- Materials for H₂ storage
- Materials for Solar Energy utilization (Photovoltaic cells)
- Thermoelectric materials
- High purity materials
Material issues in SOFC technology

- Poor sinter-activity of Electrolyte and Inter-connect materials: Role of Nanoscience
- Design of new Ionic conductors based on structure-property correlation (for Low Temperature-SOFC)
- Design of new cathode and anode materials

An optimum degree of disorder leads to highest ionic conductivity in a system

Brownmillerite $\text{Ba}_2\text{In}_2\text{O}_5\square$ (Ordered lattice)

$\text{Ba}_2\text{In}_{2(1-x)}\text{Ti}_{2x}\text{O}_{5+x}\square_{1-x}$ (Disordered perovskite)
Iodine-Sulfur process for $H_2$ production (material-related challenges)

**Materials for $H_2SO_4$**
- Liquid phase at low temperatures: Hastelloy B, Incoloy 815, Alloy 20 and in some cases AISI 316
- Liquid and Vapour phases ($300 < T < 400 \, ^\circ C$): Refractory bricks
- Vapour phase ($400 < T < 900 \, ^\circ C$)
  - Incoloy 800 (Maximum temperature 900 °C) and AISI 310 (Maximum temperature 700 °C)
- Ceramics like $Al_2O_3$, $ZrO_2$, $SiC$, $Si_3N_4$, and $SiSiC$
- Fe-Si alloy ($Si > 13\%$) – Low Si core and high Si surface

**Materials for $HIx$**
- Zirconium, tantalum, Durichlor 51, and Hastelloy B2

**Challenges**
- Development of new materials, fabrication technologies, coatings & compatibility trials with acids

**Equations**
- $2HI + H_2SO_4 \xrightarrow{120^\circ C} I_2 + SO_2 + 2H_2O$
- $2HI \xrightarrow{450^\circ C} H_2 + I_2$
- $H_2SO_4 \xrightarrow{850^\circ C} H_2O + SO_2 + 1/2 O_2$

**Diagram:**
- H$_2$SO$_4$ Decomposition
- Bunsen reaction
- HI Decomposition
BARC has developed a high current density compact electrolyser (10 Nm$^3$/hr of Hydrogen capacity)

- A 40-cell electrolysis module (weighing 900 kg) incorporating porous nickel electrode operates at a high current density of 4500 ASM (amperes per square metre of electrode area) which is much higher than conventional cells in the market (operates at 1500 ASM or below)

- The electrolyser produces 10 Nm$^3$ of hydrogen and 5 Nm$^3$ of oxygen per hour at a temperature of 55 °C and at a pressure of 0.16 MPa
Nano-materials for hydrogen storage

1. Inter-metallic hydride systems (Fe-Ti etc.)
2. Carbon nano-tubes
   - Multi wall Carbon NanoTubes (CNT) synthesised by Catalytic Chemical Vapour Deposition (CCVD) on different catalyst structures like Nickel Formate, Cobalt Formate etc. at 700 °C
   - CNT content of 86% achieved
   - Gas used: Acetylene-Nitrogen (600 - 900°C)
Molecular electronics: New functional molecules containing sigma and pi groups will be designed and synthesized and their Electrical characteristics will be studied for fabrication of rectifiers, negative differential resistance and memory devices.

Fig.: 5-(4 undecenyloxyphenyl)-10,15,20-triphenylporphyrin (TPP-C11) designed and synthesized earlier at BARC shows hysteresis and memory effect.

Thermoelectric devices

• Devices based on PbTe with 6% efficiency prepared with upto 16 elements.

• Larger devices will be prepared in 2009 to get voltages of above 1.5 V, with improved packaging.
Czochralski Crystal Pullers at BARC

- Growth of single crystals of LiTaO$_3$, an important ‘Smart Material’, will be taken up for device development.
Solid State Chemistry

- Perovskites $\text{ABO}_3$
- ABO$_4$ structure
- Fluorites $\text{MO}_2$
- Pyrochlores $\text{A}_2\text{B}_2\text{O}_7$
- Spinels $\text{AB}_2\text{O}_4$
- Aurvillius Phase $[\text{Bi}_2\text{O}_2]^{2+} [\text{A}_{m-1}\text{B}_m\text{O}_{3m+1}]^{2-}$
- Inorganic fluorides
- Framework solids
Aurivillius phases

(ferroelectric materials)

Intergrowth (layered) compounds of the perovskite and fluorite lattices

\[[M_{2}O_{2}]^{2+} [A_{m-1}B_mO_{3m+1}]^{2-}\]

\(M = Bi^{3+}\)

\([A_{m-1}B_mO_{3m+1}]^{2-}\) perovskite slab

\(m = \text{thickness of perovskite slab}\)

\(m = 2\) \(Bi_4Ti_3O_{12}\)

\(m = 6\) \(Bi_7Ti_3Fe_3O_{12}\)
Multiferroic Materials

Coexistence of two or more than two ferroic ordering
(magnetic $M_s$, electric $P_s$ and strain $\varepsilon_s$)

• Most of the existing multiferroic materials are Antiferromagnetic (AFM) and Ferroelectric (FE)

• Need of the hour: Materials with Ferromagnetism (FM) and Ferroelectricity (FE)
  (Antagonistic combination)

Aim?
- Better understanding
- Higher value of polarization
- Coupling effects
- Pb free compounds

How to achieve this combination (FE/ FM coexistence)?
- Crystallographic approach
- Chemical approach
- Composite approach
- Core-shell configuration
Ba and Mn co-doped BiFeO$_3$ system with coexistence of FE and FM

Preparation: Xerogel method

TEM and SAED patterns of $\text{Bi}_{1-x}\text{Ba}_x\text{Fe}_{1-y}\text{Mn}_y\text{O}_3$

Magnetization with Field

Electric polarization with Field
Spintronics materials

Prerequisites

- Wide band gap semiconductor host lattice (2 to 4 eV)
- Charge carrier density (about $10^{20} / \text{cc}$)
- Appreciable solubility of transition metal ions

Common host materials
ZnO (3.37 eV)
In$_2$O$_3$ (3.79 ev)
TiO$_2$ (3.2 eV)

Common dopants
Mn, Co, Fe, Cr

Co-dopant: Li
1D morphology
Stabilization after Li substitution in ZnO (template free)

Zn acetate, Co acetate, Li acetate heated in try-octylamine at 320 °C.
First principle theoretical modeling (DFT)

(a) Zn$_{0.97}$Co$_{0.03}$O  (b) Zn$_{0.91}$Co$_{0.03}$Li$_{0.06}$O

Demonstrating strong relaxation effects due to presence of Li substitutional Dopants, which restores the 1D morphology

Magnetization data at RT

ZnO (Diamagnetic)
Zn$_{0.90}$Li$_{0.10}$O (Diamagnetic)
Zn$_{0.97}$Co$_{0.03}$O (FM)
Zn$_{0.95}$Co$_{0.05}$O (FM)
Zn$_{0.85}$Co$_{0.05}$Li$_{0.10}$O (Enhanced FM)
Ink-jet printed oriented ZnO:2%Co Film

ink jet printed highly (002) axis oriented ZnO film on Si

1 pass 1 time dried at 180 heated at 500 15 min.
1 pass 2 times dried at 180 heated at 500 15 min. after each pass
1 pass 3 times dried at 180 heated at 500 15 min. after each pass
1 pass 3 times dried at 180 heated at 500 15 min. only once finally

Best oriented Film of Co2%:ZnO

M vs. H at RT shows ferromagnetism

Different patterns printed on different substrates

Polyimide

Silicon

RT
Tb, Dy doped Gd$_2$O$_3$: A white light emitting material

Based on the CIE coordinates and CCT values, double doped Gd$_2$O$_3$ (Tb; 0.05, Dy; 1.95%), when excited at 247 nm, emits white light, which is closest to the standard noon daylight.
Studies of Nanostructures for Gas sensing

• Role of intra-grain and grain boundary characteristics of oxide nano-structures will be investigated to develop more sensitive and selective gas-sensors.

• Studies will use nanowires, nano-heterostructures of different materials as SnO$_2$, CuO, In$_2$O$_3$, ZnO etc that have already been prepared. (Figures below show a few nanostructures and single wire sensor)

Te nanotubes  ZnO tetrapods  Nano-heterostructures: WO$_3$ on SnO$_2$  Single nanowire sensor
**Condensed Matter Research - Bulk, Nano, Amorphous…**

**Single Crystal**
- Bright-field electron micrograph
- Single crystal embedded in amorphous matrix of Zr based glass.

**Quasicrystal**
- Exhibits five fold symmetry
- Electron diffraction pattern of as-grown Al₆CuMg₄

**Nanocrystal**
- TEM image of γ-Fe₂O₃ Nanoparticles

**Nanowire Thin Films**
- SEM micrograph of ZnO

**Amorphous ribbons**
- Electron Diffraction
- Amorphous Zr-35 at % Ni ribbon
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