Abstract
Few selective glass & glass-ceramics having potential applications in the field of sealing, high voltage and high vacuum, energy storage/battery, bio-medical, consumer items, nuclear and optical were developed. Among these, machineable quality magnesium alumino-silicate(MAS) glass-ceramics were developed through glass route, the flow sheet for the preparation of rods, cylinders and discs were demonstrated. The material developed has been successfully used for the fabrication of high voltage (breakdown voltage 220-250kV/cm) and UHV compatible components for cascade plasma gun, furnace insulation and many other applications for different users within DAE. For fabrication of matched type glass-ceramics to metal/alloys seals, lithium zinc silicate were synthesized and characterized for their compatibility with different metals/alloys. Structural studies of the LZS glass and glass-ceramics using $^{31}$P, $^{11}$B, $^{27}$Al, and $^{29}$Si solid state NMR helped in accurate quantification of different phases present in the glass and glass-ceramics. Development of chemically durable phosphate glasses for matched type seals for low melting metals /alloys, like Al/Be alloys, and glasses for high temperature sealing application, especially for use as SOFC sealant (seals fabricated with Crofer interconnect material withstood vacuum of $10^{-6}$ Torr at RT-800$^\circ$C) were also carried out. Recent development of phosphate glass-ceramics based Li-supersonic conductor for Li-Air rechargeable battery showed a high conductivity value of $2-3 \times 10^{-4}$ S/cm at RT. Thin sheets of this materials are being prepared by tape casting for miniaturization of the devices. Development of Yttria-alumino-silicate (YAS) based glass microsphere for radiotherapy application, surface modification of glasses for improved functionality i.e. toughening of glasses by chemical ion exchange process and super-hydrophobic glass using a novel process of spinodal decomposition also carried out.

Introduction
Glass/Glass-ceramics find applications in various technological fields including vacuum, high voltage, electronics, nuclear, space, biomedical, safety gadgets, energy conservation, optical etc. The most interesting aspects of working on glass/glass-ceramics is that even though they are multi-component materials, their properties can be controlled, thus developing tailor made products for use in technical fields. Moreover, glass-ceramics have considerable advantages over other materials such as glasses, ceramics, metals and polymers. Therefore, glass/glass-ceramics are used in almost every discipline of science, technology and engineering now days. We have developed few important glass and glass-ceramics having potential technological applications in various fields. Among theses, magnesium-aluminum-silicate (MAS) belongs to a special class of technologically important advanced ceramics having applications in the areas related to ultra high vacuum, high temperature, high voltage etc. The unique feature of MAS glass-ceramic is its machineability, i.e. the material can be transformed into desired shape and size by machining to precise tolerance and surface finish with conventional carbide tipped tools. Lithium zinc silicate (LZS) glass-ceramic is another technological important glass--ceramics materials which finds incredible applications in the field of sealing technology. The special features of this materials are wide glass forming region and tuneable thermal expansion characteristics. The thermal expansion coefficient of LZS...
glass-ceramics can be varied in a wide range from $50 \times 10^{-7}$ to $200 \times 10^{-7}$ °C in controlled manner and thus, found suitable for preparation matched type of hermetic seals with a variety of metals/ alloys. In addition, this material also shows superior insulation, higher mechanical strength and good chemical durability. Application of phosphate glasses are limited due to moisture sensitiveness of these glasses. However, phosphate glasses having different additives were found to show better stability under ambient conditions and are extensively used for various applications. Phosphate glasses generally have lower glass transition temperatures and higher thermal expansion coefficients compared to silicate and borate glasses and so are prime materials for glass-metal sealing applications especially with low melting and high expansion coefficient metals like Al, Cu etc. It may be mentioned that Al and Al alloys are important materials for space applications because of lower weight and cost and desired mechanical properties. Alkaline earth silicate glass/glass ceramics are found to be promising candidates for uses as high temperature sealant especially for SOFC application. They shows acceptable long term thermal, mechanical and chemical durability with other electrode materials in oxidizing and reducing atmosphere.

Apart from sealing glass/glass ceramics, phosphate glass-ceramics based on NASICON structure shows potential application as solid state electrolyte in energy storage devices/batteries. They have higher ionic conductivity at RT and thermal and chemical stability compared to liquid and polymer based electrolyte. Uses of glass/glass-ceramics in the field of biomedical as bone/teeth filler, replacement of damaged bone parts and drug delivery are well known. $^{90}$Y-a beta emitter in an irradiated $Y_2O_3$-$Al_2O_3$-$SiO_2$ (YAS) glass microsphere with a half life period of 64hrs and about 934 KeV energy found very useful for localized radiotherapy treatment of hepatic cellular carcinoma(HCC) and synovitis. In addition to improve the properties of glasses modification of surface to enhance hydrophobicity on glass surface and toughening of glass by chemical ion exchange process found useful for use of these materials in many strategic applications.

**Machineable (Magnesium Alumino Silicate) MAS glass ceramics:**

For the preparation of magnesium alumino silicate(MAS) glass-ceramics with superior machineability, the composition and process conditions were optimized to precipitate requisite amount of the micaceous phase and obtain a cross-linked microstructure that provides a break down strength of $220 – 250$ kV/ cm, micro hardness of 2.56 GPa and outgassing rate $7.9 \times 10^{-9}$ Torr cm$^{-2}$ sec$^{-1}$. The flow sheet for the preparation of rods, cylinders and discs of machineable MAS glass-ceramic was developed through a comprehensive optimization of the composition and process conditions. The machineability of the material was elicited by the smooth sectioning of the wafers of 200-500micron thick using a diamond wheel. The dielectric properties of this material studied over a wide frequency range showed low loss at high temperature. Optimization of the composition was achieved through structural information obtained using $^{27}$Al and $^{29}$Si solid state NMR. MAS glass-ceramic in the form of rods (40mm dia X 120mm L), cylinders (60mm OD, 40mm IDX120mm L), discs (70mm dia X 25mm thick) have been developed. A number of glass/ glass-ceramics developed are widely used for fabricating seals, feed throughs, spacers, lugs and other components for use in different applications within and outside DAE.
Lithium Zinc silicate glass ceramics:

Glass-ceramics of the lithium zinc silicate (LZS) system are a versatile class of materials having application in hermetic sealing with various metals including stainless steels and Ni based super alloys. Development of lithium zinc/aluminum silicate glass-ceramics with tuneable thermal expansion coefficient were carried out for sealing with Cu and SS321. Thermal expansion coefficient of LZS glass-ceramics was tuned by optimizing the glass composition and process parameters. For establishing the process parameters, the in-situ crystallization during heating and cooling cycles was studied. Optimization of bonding at seal interface was established by microstructural studies using SEM-EDX. Single/ multi-pin hermetic seals fabricated with LZS glass-ceramic have withstood vacuum levels of 10^{-6} Torr with a low leak rate of 10^{-9} Torr litre sec^{-1} and pressure upto 13000 psi. Several such seals have been supplied to various users in BARC.

Structural studies using solid state MAS NMR:

Extensive studies on structural aspects of LZS glass and glass-ceramics using \(^{31}\)P, \(^{11}\)B and \(^{29}\)Si solid state MAS NMR were carried out to determine the structural units of Si, Al, P and B, the coordination number and neighbouring atoms, the crystallization behaviour, the effect of phase separation on nucleation and accurate
quantification of crystalline phases in glass-ceramics. These investigations have helped in demystifying the structure-property correlation in this glass-ceramic system and also to improve the material quality.

Sodium-boro-phosphate glass:
Chemically durable Na$_2$O-BaO-B$_2$O$_3$-P$_2$O$_5$ glasses were developed for sealing with low melting materials such as, Al/Be alloys. The flow sheet for preparation of phosphate glasses with matched thermal expansion and high chemical durability was carried out by the optimization of composition and process parameters. Various constituents like, barium, phosphorus, and boron, were added in proportionate amounts to tune the thermal expansion coefficient value and to improve the chemical durability. The structure-property correlation in these glasses was obtained from studies conducted using $^{27}$Al and $^{31}$P solid state NMR. The glass composition was further optimized by evaluating the chemical durability in various mediums at room temperature and at elevated temperature. Seals fabricated with the optimized composition demonstrate leak tightness upto $10^{-8}$ Torr.

Barium alumino-silicate glasses for SOFC application:
Alkaline-earth silicate based glasses were prepared for prolonged use at high temperature under dry and wet H$_2$ atmosphere. The glass composition was optimized for matched thermal expansion co-efficient with Crofer 22 interconnect and other components of electrolyte cell. Further, various parameters such as, flow temperature, wet ability and adhesion of these glasses with the metal interconnect and cathode materials were evaluated for compatibility. Seals fabricated with the metal interconnect was found to withstand a vacuum of $10^{-6}$ torr at RT as well as at 800°C. Chemical stability of the seal was tested at 800°C for 2000hrs. Interface studies showed inter-diffusion of Ba, Ca, Al, Si and Fe elements and enrichment of Cr at the sealing interface, which is responsible for the good bonding in these seals.
LATP glass ceramics for Li-air rechargeable battery:
The development of Li₂O-Al₂O₃-TiO₂-P₂O₅ glass-ceramics for use as Li-superionic conductor in Li-Air rechargeable battery has been recently initiated. The flow chart for preparation of glass-ceramics with NASICON structure was carried out by the optimization of composition and process parameters. The optimized LATP glass-ceramics show electrical conductivity value of 2-3 x 10⁻⁴ S/cm at RT with very good interconnected LATP microstructure. Thin thin sheets of this materials are being prepared by tape casting for miniaturization of the devices.

Cole-Cole plot for LATP fast ionic glass-ceramics.

Yttrium-alumino-silicate(YAS) glass microsphere for radiotherapy application:
Y₂O₃-Al₂O₃-SiO₂ based glass microsphere finds potential application in radiotherapy treatment of hepatic cellular carcinoma(HCC) and synovitis. ⁹⁰Y-a beta emitter in a irradiated YAS glass with a half life period of 64hrs and about 934 KeV energy found very useful for localized cancer treatment. Microsphere in the range of 10-50µm have been successfully prepared by flame pyrolysis process. Attempts are now being made to prepare monodispersed microspheres and YAS glass with high yttrium content for higher efficiency.

SEM image of Y₂O₃-Al₂O₃-SiO₂ glass microsphere.

Development of Superhydrophobic glass by spinodal decomposition
Work has been initiated on enhancing the superhydrophobicity of glasses through creating nano-scale structure on the glass surface. This has been achieved through a novel process of spinodal decomposition on nano-metric scale followed by etching. Glasses based on Na₂O-B₂O₃-SiO₂ system were prepared by melt-quench technique and heat treatment schedule was optimized for a fine scale interconnected
microstructure. SEM showed uniformly distributed interconnecting microstructure after heat treatment at 700°C/1h. Samples were etched for a controlled surface modification to enhance the hydrophobicity of the glass surface.

**Toughening of glass by chemical-ion exchange process**

Toughened glasses find potential applications in many fields including aeronautics as cockpit windows, mobile screen/ touch screen, transparent armor, glass substrates for harvesting solar energy etc. Initial work on processing of toughened glass using ion exchange process has been successful. Thin sheets of sodalime glass were treated in molten KNO₃ bath for chemically exchange of the K⁺ ion in place of Na⁺ ion, which induces compressive stress on the surface and increases the toughness. The distribution of the stresses and densification of structure are under investigation using mico/nano-indentor and micro-Raman spectroscopy.

**Other Glass and Glass-Ceramics**

In addition to above, the development of rare earth doped Yttria-alumino-silicate (YAS) glass/glass ceramics for white LED application, transparent Magnesium alumino-silicate (MAS) glass-ceramics for optical/laser applications, dosimetry glasses and hollow Hydroxyapatite(HAP) for drug delivery are being carried out.

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**Reference**