Synopsis

**Processing of Bulk Metastable Oxide Ceramics**

Oxide ceramic materials are extensively used in various modern application domains which require properties such as high temperature stability or creep resistance, wear resistance, chemical stability, useful electronic, optical and magnetic properties. In the diverse arena of materials technology that interlinks processing, structure, properties and performance, the advancement of new processing techniques to develop oxide ceramics facilitates the extension and refinement of their desirable properties and also mitigate their limitation in terms of application. Progress in processing science/technology offers a real impetus to the development of metastable ceramics with novel, non-equilibrium structures that exhibit scientifically interesting properties and have the potential to cater to the requirements of modern application areas.

In the absence of the equilibrium state of a material system, metastable states can be formed with amorphous phases, extended solid solutions, metastable crystal structures and nanocrystallinity. Such metastable states can be retained by imposing kinetic constraints, which means that under the conditions of temperature and pressure, atomic mobilities are inadequate for the transformation. Metastable ceramics that are produced using non-equilibrium processing routes, such as rapid solidification, vapour deposition, spray pyrolysis, sol-gel technique etc., have been known to possess potentially useful properties, such as hard and soft magnetic characteristics, semiconductivity, varistor action, optical transmittivity and superconductivity. Apart from possessing attractive properties, a metastable phase may also serve as a precursor to a desired microstructure; for instance, controlled crystallization of an amorphous phase is a possible way enroute to nanocrystalline structure.

It was well recognized that the comprehensive study and use of nanostructured and other metastable ceramics requires consolidation of the fine discontinuous forms (powders or flakes) produced from non-equilibrium processing routes, into bulk shapes with greater control on the fine scale of the structure. Such efforts have not been entirely successful.
Non-equilibrium processing techniques do not produce the metastable materials in bulk form. Consolidation of metastable ceramics into dense forms needs high temperatures, mechanical activation (in the form of static pressures or shock waves), or a combination of both. Such activation may trigger the transformation of the desired metastable phase into a more stable phase with concurrent grain growth. Conversely, conditions that allow the desired metastable phase to be retained may not be adequate for complete densification.

The subject of the present thesis is two-fold: (i) processing of dense amorphous Al$_2$O$_3$-Y$_2$O$_3$ materials through a novel densification route involving hot pressing of amorphous powders, produced by co-precipitation, at low temperatures and moderately high pressures, (ii) detail study of possible deformation mechanisms of the amorphous phase from mechanical testing at elevated temperatures. Unusual deformation behavior of the bulk amorphous material has been related to the densification process.

**Development of Pressure Consolidation Technique**

Amorphous powder of composition Al$_2$O$_3$-15 mol% Y$_2$O$_3$ (A15Y) was synthesized by co-precipitating a hydroxide from metal nitrate precursors solution by using ammonium hydroxide. Chemical homogeneity was ensured by a molecular level mixing of precursors of aluminium and yttrium at room temperature. The as-precipitated powder undergoes thermal decomposition (pyrolysis) to an amorphous oxide by ~770-800$^\circ$ C. The crystallization temperature was found from thermal analysis to be ~900$^\circ$ C, with $\gamma$-Al$_2$O$_3$ as the initial product of crystallization. The true density of the amorphous A15Y phase was measured to be only 2.69 g cm$^{-3}$ by pycnometry, which is ~2/3 of the assemblage of equilibrium crystalline phases consisted of Al$_2$O$_3$ and YAG.

Uniaxial hot pressing was performed with decomposed, classified powders (large agglomerates with sizes more than 10 $\mu$m were removed by sedimentation technique) at low temperature of about 630-640$^\circ$ C and moderately high pressure of 710-750 MPa. Pressure was held constant for 30-45 minutes. Cold compaction at pressures of 50-65 MPa for 8-10 minutes was carried out prior to hot pressing to ensure green strength of the compacts. All hot-pressed compacts revealed significant densification (95-96% relative
densities) with uniformly distributed fine porosity. X-ray diffraction, electron microscopy analysis, Raman spectroscopy and differential thermal analysis established the amorphous nature of the dense, hot-pressed pellets. The amorphous phase displays an elastic modulus of ~ 50-60 GPa and a hardness of 4-5 GPa, which are considerably lower than those of the crystalline counterpart.

**Deformation Behavior of Amorphous Al$_2$O$_3$-Y$_2$O$_3$**

The experiments described above clearly demonstrated the feasibility of producing bulk metastable ceramics in the Al$_2$O$_3$-Y$_2$O$_3$ system by a novel consolidation (viz., low temperature-high pressure) route of amorphous powders. This section of the thesis concentrates on studying the deformation mechanisms of the amorphous phase, which are found to be characteristic of the temperature domain of the experiment. Uniaxial compression tests at temperatures of 650-850$^\circ$ C with constant engineering strain rates of $\sim$3-4 X $10^{-4}$ s$^{-1}$ were conducted on dense amorphous samples made from the hot-pressed compacts.

At a temperature of 850$^\circ$ C, i.e., close to the crystallization temperature, the amorphous phase was characterized by homogeneous deformation with continuous work hardening after yielding, accompanied by an increase in the true density of this glass by 10-12%. X-ray and electron microscopy analysis confirmed that the density increase was not due to the formation of nano-crystals at this high temperature. Raman spectroscopy and differential thermal analysis further corroborates that the glass was amorphous even after deformation. No shear instabilities were formed at the side surfaces due to the deformation. Significantly large compressive longitudinal strains up to about 28% were observed before unloading. Moreover, an interrupted loading-unloading test established that the bulk density increase was monotonic with the existence of multiple amorphous states enroute to a succession of denser structures. A simultaneous increase in both hardness ($H$) and modulus ($E$) of the amorphous phase of up to 100% after deformation bolstered this experimental observation of bulk density increment at constant porosity. The above evidence clearly points towards significant structural changes of the amorphous phase during high temperature deformation process and therefore a phenomenon of molecular densification of the amorphous structure.
through a hierarchy of dense amorphous phases was hypothesized, analogous to density or entropy driven amorphous-to-amorphous phase transitions (*polyamorphism*). Note that the densification described here does not refer to the conventional removal of porosity in a ceramics.

At an intermediate temperature of 725° C, which is significantly (~200° C) below the crystallization temperature, plastic deformation commences at a stress (yield stress) of 700-780 MPa (considerably higher compared to the yield stress at 850° C) and continued to deform plastically with a slowly decreasing flow stress before reaching a plateau. Thus, the glass exhibited *flow softening*, in contrast to flow hardening observed at 850° C. Plastic deformation of this glass is largely *non-viscous* through shear instabilities (akin to the low temperature deformation behavior of metallic glass) and resulted in 8% increment in bulk density after deformation. Once again, the amorphous nature of the glass after deformation was confirmed by X-ray and electron microscopy analysis. Therefore, this intermediate temperature domain was characterized by both densification and shear.

Deformation at even lower temperature, viz., at the temperature of hot pressing (650° C), was also characterized by elastic-plastic behavior (similar to flow softening described above), with immediate yield drop after yielding and resulted in a fairly large amount of plasticity of about 17% before unloading. The bulk density was found to be increased only by 2%.

Another very interesting experimental finding from the present investigation is the time-dependent deformation (viz., creep densification) exhibited by this glass. It was established from the result of longer term creep experiment at 850° C that the glass revealed large uniaxial compression of about 15% with 5.5% densification to a density of 3.02 g cm⁻³. Strain rate sensitivity of the A15Y glass was revealed by another stress jump test.

To summarize, the present thesis elucidates the discovery of a new class of ceramics with unusual physical properties in an amorphous mixture of Al₂O₃-Y₂O₃, which is in contrast to the conventional brittle ceramics. This new class of ceramics deforms plastically without any hydrostatic containment, like ductile metal, at temperatures about 1000° C below those
at which their crystalline counterpart would deform. The behavior of this amorphous ceramics under stress that leads to unusually large change in shape, density, hardness and modulus with hierarchies of amorphous structures is demonstrated in detail with experimental evidence.