1.1 INTRODUCTION

To define glass as an inorganic product of fusion is to exclude the glasses obtained by sol-gel method. To include the gel-derived glasses, Mackenzie's definition that glass is a noncrystalline solid seems to be more appropriate. And although a glass produced in a beaker(by gelation)can never be the same as one produced in a crucible(by melting), one still talks about the sol-gel(SG) method which has emerged as an alternative(sic) to conventional glass melting. To put any doubt about the viability of gel-derived glasses at rest, one only needs to refer to the preparation of transparent high-silica glass articles, such as radomes, from colloidal gels[1,2].

A glass can be obtained either by freezing the liquid structure of its melt or by arresting the same random structure present in the solution by means of gelation followed by the removal of volatiles from the gel to produce a glass.

The SG technique has also been extended to prepare crystalline ceramics with exceptional microstructure[3]. Following SG route, it is possible to prepare Na_2O-ZrO_2-SiO_2 glasses with unusally high ZrO_2 contents[4] or CaO-SiO_2 glasses within the miscibility gap[5] because glasses are formed by a low temperature viscous sintering process rather than by cooling a melt and thereby avoiding the limitations imposed by the critical cooling rate for glass formation. However, SG glasses have a strong crystallisation tendency[6] than the equivalent glasses made by melting. Avoidance of crystallisation is vital to permit formation of glass at temperature below the liquidus.

1.2 CLASSIFICATION OF GELS

It is necessary to define the terms sol and gel before going to describe the SG process. A sol is a disperse system where the dispersed phase, consisting either of solid, discrete 'globules' or oligomers in the form of chains is present in a liquid dispersion medium. The medium can be water or any other liquid. A gel is a stiff mass of continuous disperse phase still in the liquid medium.

1.3 MECHANISMS OF GELATION

There are two basic types of mechanisms, namely the colloidal and polymeric, leading to gelation. In colloidal system, discrete colloidal particles are linked together into branched chains which form extensive network throughout the liquid medium by a mechanism similar to flocculation. The interparticle distance at the gelling point, which may be affected by the addition of electrolytes, influences the capacity of the gel to remain monolithic during the transformation to an organic free state. On the other hand, gelling in polymerised systems occurs as a result of polymerisation by chemical reaction. The nature and the kinetics of the reactions determine the properties of the gel and resultant inorganic polymer. Usually, under base catalysed conditions, colloidal particles are formed and an acid-alcohol solution favours the formation of polymerisable species.

Although the present work does not deal with colloidal gels, a comparison of their properties with the properties of polymeric gels (subject of study) may be a useful exercise. Colloidal gels are rheologically similar to soils, which are plastic materials, exhibiting a yield stress that depends on the moisture or the liquid content. On the other hand, a polymeric gel behaves like a visco-elastic material and changes from viscous to elastic nature with progressively decreasing volatile content. Colloidal gels are weak in shear and behave like a thixotropic liquid suggesting that the gel network is composed mostly of relatively weak physical bonds rather than primary chemical bonds. In the case of polymeric gel, the disruption of its structure is irreversible.

There are other distinguishing features between the colloidal and polymeric gels. While the former can take place in a non-aqueous medium[7], presence of water is essential in the latter. Also, a colloidal gel may densify by expelling the liquid from its structure while in the case of polymeric gel, the solvent has to be allowed to evaporate.

It is possible to produce glasses having the same composition following either of the above two mechanisms. For example, transparent silica monoliths can be prepared either by the acid hydrolysis of tetraethyl orthositicate (TEOS) or from colloidal gels using fumed silica and either water or various non-aqueous media (having various volatility) as starting materials or by a combination of both the mechanisms[1]. High silica glasses having properties comparable with fused silica have been prepared from colloidal gels[1,2].

1.4 POLYMERIC SILICA GEL

TEOS, which shows less vigorous hydrolysis than other metal alkoxides, is immiscible with water but soluble in ethyl alcohol. It hydrolyses rather slowly and even in excess of water it does not hydrolyse completely.

$$Si(OEt)_4 + H_2O \rightarrow SiO_{\frac{4-x-y}{2}} (OH)_x (OEt)_y + EtOH \quad ..(1.1)$$

where x and y are small fractions and Et denotes ethyl(C_2H_5) group.

In alcoholic medium, a small amount of OEt keeps the silica complex, which finally produce the gel, soluble.