Chapter-II

PREPARATION OF GLASS BY SOL-GEL METHOD

2.1 INTRODUCTION

As pointed out in Chapter - I, the conventional method of preparation of glass is by rapid quenching of the melt Recently [Dislich (1971), Schroeder (1978), Mukherjee et at (1976)] a new method called the sol-gel method was developed to prepare glass The method basically involves two stages, namely, the preparation of gel and the transition of gel into glass

The preparation of gel can be achieved by two methods The first method is by hydrolysis and polycondensation of alkoxides The second is by colloidal method In the first method gel preparation results from the chemical reaction which is irreversible Glass-like network is formed during gelation at room or slightly elevated temperature Addition of other components can easily be done in this method In the second method, gelling results from the hydrogen bond formation between colloidal particles and a solvent The reaction is reversible Here the glass-like network is formed only during sintering This method has the limitation in that only a few additional components like B_2O_3, P_2O_5 and GeO_2 can be introduced into the silica glass

2.2 GEL PREPARATION BY HYDROLYSIS AND POLYCONDENSATION

Ebelmen (1846) was the first to prepare gel by this method He demonstrated that a solution of tetraethoxysilane in water leads to the formation of the gel of single oxide Following this, other workers (for example,

Friedel et al (1865, 1867, 1868) have prepared gels using tetraethoxysilane as one of the components

2.2.1. Chemistry of the Gel

The reaction involves the polymerization (hydrolytic polycondensation) of alkoxysilane with other metal alkoxides or with suitable metal salts to produce a multicomponent non-crystalline transparent "glass-like" gel The network is like Si-O-M-O-Si where M is a metal atom such as Al, Ti or B

In the process of polymerization one defines the "gel point" as the stage at which the solution mixture transforms from a viscous liquid to an elastic gel At the gel point, the generation of an infinite network commences abruptly As the degree of polymerization increases beyond the gel point, the relative proportions of the "sol" to "gel" decreases continuously and the network grows rapidly The schematic diagram of the process is shown in (fig 2 1)
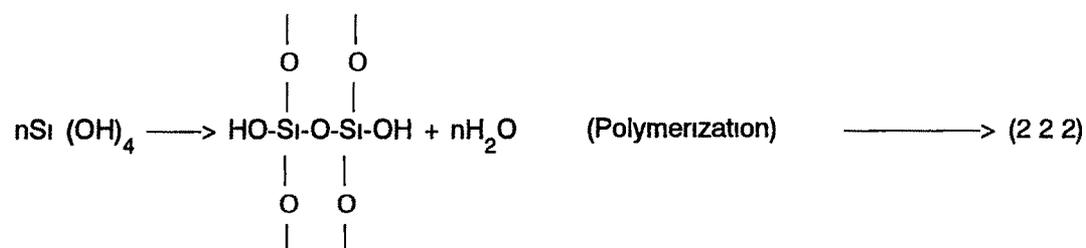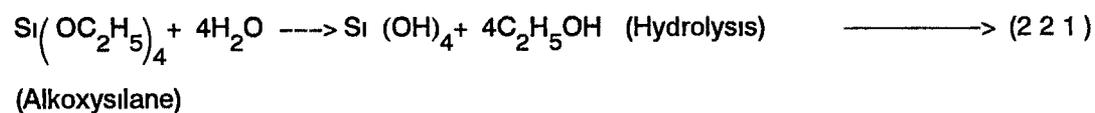
.Alkoxysilane (A)

Metal Alkoxide (MA)*

.A + MA

.A + Metal Salt

Solvent
———————>

Homogeneous

Solution (sol)

Hydrolytic
———————>
Polycondensation

Multicomponent

homogeneous

non-crystalline gel

*Mixture of at least two metal alkoxides

Fig: 2.1 – Sol-Gel Process (Alkoxide Method)

The process of hydrolysis and polymerization of alkoxides can be illustrated by the following examples
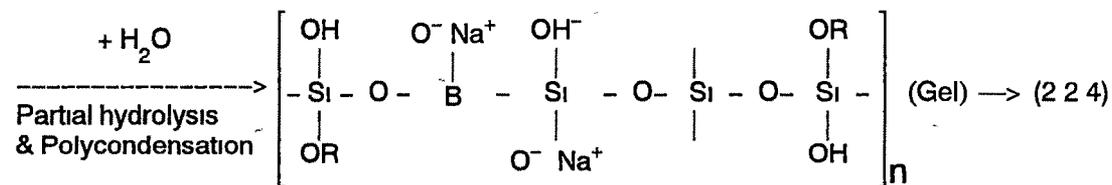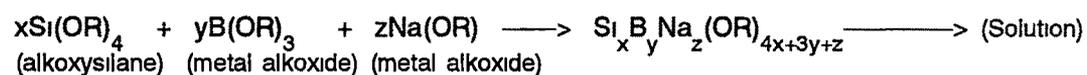
Example - 1:

$$Si\left(OC_2H_5\right)_4 + 4H_2O \longrightarrow Si\ (OH)_4 + 4C_2H_5OH \quad \text{(Hydrolysis)} \longrightarrow (2\ 2\ 1\ )$$
(Alkoxysilane)

$$nSi\ (OH)_4 \longrightarrow HO-\overset{\overset{\displaystyle |}{\underset{\displaystyle |}{O}}}{\underset{\overset{\displaystyle |}{O}}{Si}}-O-\overset{\overset{\displaystyle |}{\underset{\displaystyle |}{O}}}{\underset{\overset{\displaystyle |}{O}}{Si}}-OH + nH_2O \quad \text{(Polymerization)} \longrightarrow (2\ 2\ 2)$$

In short, the reaction can be written as,

$$Si(OH)_4 \longrightarrow SiO_2 + 2H_2O \longrightarrow (2\ 2\ 3\ )$$

The above two reactions (2 2 1) and (2 2 2) take place simultaneously

Example - 2:

Multicomponent Gel :

$$xSi(OR)_4 + yB(OR)_3 + zNa(OR) \longrightarrow Si_xB_yNa_z(OR)_{4x+3y+z} \longrightarrow \text{(Solution)}$$
(alkoxysilane) (metal alkoxide) (metal alkoxide)

$$\xrightarrow[\substack{\text{Partial hydrolysis} \\ \text{\& Polycondensation}}]{+H_2O} \left[-\overset{\overset{\displaystyle OH}{|}}{\underset{\overset{\displaystyle |}{OR}}{Si}} - O - \overset{\overset{\displaystyle O^-Na^+}{|}}{\underset{\overset{\displaystyle |}{O^-\ Na^+}}{B}} - \overset{\overset{\displaystyle OH^-}{|}}{Si} - O- \overset{\displaystyle |}{Si} - O- \overset{\overset{\displaystyle OR}{|}}{\underset{\overset{\displaystyle |}{OH}}{Si}} - \right]_n \text{(Gel)} \longrightarrow (2\ 2\ 4)$$

(R is the alkyl group and x, y, z are in moles)

Example - 3 :

$$Si(OC_2H_5)_4 + 4H_2O \longrightarrow Si(OH)_4 + 4C_2H_5OH \qquad \longrightarrow (2\ 2\ 5)$$
(alkoxysilane)

$$\equiv Si\text{-}OH + HO\text{-}Si\equiv \longrightarrow \equiv Si\text{-}O\text{-}Si\equiv + H_2O \qquad \longrightarrow (2\ 2\ 6)$$

$$NaNO_3 + H_2O \longrightarrow Na^+OH^- + HNO_3 \qquad \longrightarrow (2\ 2\ 7)$$
(metal salt)

$$\equiv Si\text{-}O\text{-}Si \equiv + Na^+OH^- \longrightarrow \equiv Si\text{-}O\text{-}Na^+ + \equiv Si\text{-}OH \qquad \longrightarrow (\ 2\ 2\ 8)$$
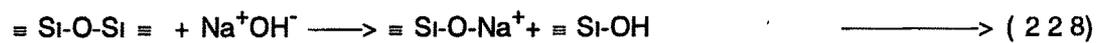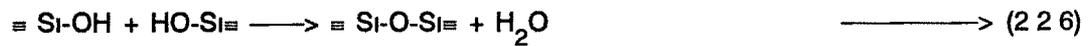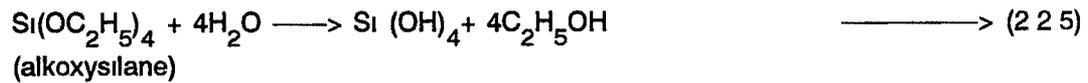
The gelling process is controlled by the following main factors chemical nature of alkoxides and other reactants, ratio of solvent to alkoxides, pH of the medium, the presence of a catalyst (acid or base), temperature, and the nature of the solvents The morphology (pore diameter and pore volume) as well as the structures of gel powders and gel monoliths are strongly influenced by the gel preparation procedure

The role of pH and the ratio of water to alkoxides are extremely important in controlling the hydrolysis and polycondensation rates This was extensively investigated by Yoldas (1975), Yamane (1979) and Sakka and Kamiya (1978) primarily in single component systems such as aluminium alkoxides, $Si(OC_2H_5)_4$ and $Si(OCH_3)_4$ The physico–chemical nature of the gel is controlled by that of intermediates which form during the hydrolytic polycondensation reactions of alkoxy-silanes and metal alkoxides The intermediates depend on the degree of hydrolysis-partial or
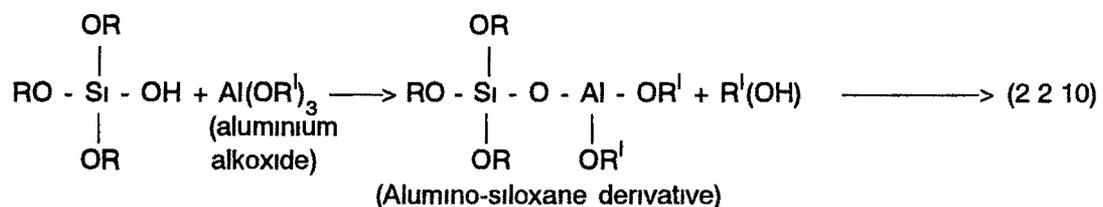
complete Yoldas (1977, 1979) Complete hydrolysis leads to precipitation and a homogeneous solution is not formed

Thus, partially hydrolysed alkoxide is suitable for the network formation For example, silicon alkoxide and alkyls may be partially hydrolysed with insufficient water to form a soluble silanol

$$
\begin{array}{c}
Si(OR)_4 + H_2O \xrightarrow[\text{hydrolysis}]{\text{partial}} \begin{array}{c} OR \\ | \\ RO - Si - OH + R(OH) \\ | \\ OR \end{array} \xrightarrow{\hspace{2cm}} (2\ 2\ 9)
\end{array}
$$

(silicon
alkoxide)

(Soluble silanol
i e ethoxysilanol)
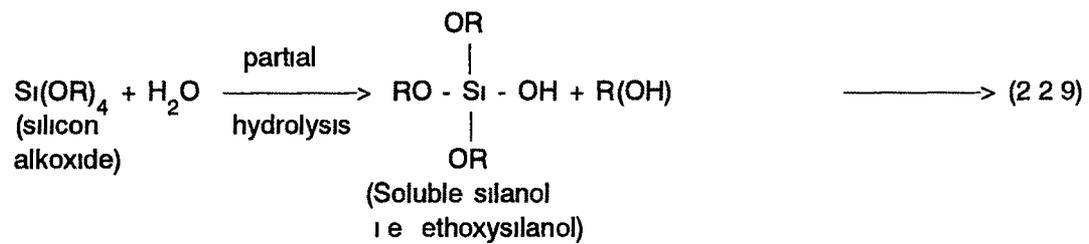
(For partial hydrolysis of an alkoxide, it is diluted with alcohol before water is added to it)

Ethoxysilanol reacts with other metal alkoxides $\left[Al(OR^l)_3 \right]$ as follows

$$
\begin{array}{c}
OR \\ | \\ RO - Si - OH + Al(OR^l)_3 \longrightarrow \begin{array}{c} OR \\ | \\ RO - Si - O - Al - OR^l + R^l(OH) \\ | \quad\quad | \\ OR \quad OR^l \end{array} \xrightarrow{\hspace{1.5cm}} (2\ 2\ 10) \\ | \quad\quad (\text{aluminium} \\ OR \quad\quad \text{alkoxide})
\end{array}
$$

(Alumino-siloxane derivative)

The alumino-siloxane derivative formed by the above reaction contains glass network formers, Si and Al, connected by oxygen Furthermore, since metallo- siloxane derivative is also soluble, it does not precipitate The addition of more water and other alkoxide causes further polymerization and cross-linking until the entire solution gels into a clear stiff single phase

Furthermore the speed of the process depends on the concentrations of acids or bases As the acid concentration increases, hydrolyzation becomes faster and condensation slower (gelation tendency is low) As the alkali concentration increases, hydrolyzation becomes slower and condensation faster (gelation tendency is high)

Thus, for preparing gel monoliths, a rapid hydrolysis is undesirable because it leads to a rapid growth of polymer and will trap Si-OH or Si-OR groups within the large three dimensional molecules where they would not further condense because of steric hindrance

Although acid catalysed hydrolysis of the alkoxides has been frequently used, base catalysis using ammonia is found to be more advantageous in producing gels with larger pores (Brinker (1982), Nogami and Moriya (1980)) Larger pores allow the condensation products to escape easily during heat treatment However, Yamane et al (1984) have pointed out some of the problems in producing gels of high purity through base catalysis These problems arise due to the rapid gelation rate (which leads to un-reacted organics) and the reduced extent of hydrolysis compared to acid catalysis Acid catalysis yields lower carbon containing gels but of a finer pore structure. Therefore, it was suggested that to produce high purity monoliths of low residual carbon, the first stage

hydrolysis is done with acid and a basic solution is added, in the second stage, to produce a gel containing large pores Such a two-step hydrolysis was followed by Kawaguchi et al (1984)

2.2.2 Non-silicate Gels

Recently, the above method has been used to obtain non-silicate gels For example, Gottardi (1982) has reported the preparation of gel using $PO(OC_2H_5)_3$ and $NaOCH_3$ Tohge and Mackenzie (1984) prepared gel using $NaOCH_3$ and tri-n-butylborate Weinburg et al (1985) synthesized gels using tri-n-butylborate and lithium methoxide

2.3. GEL PREPARATION BY COLLOIDAL METHOD

In this method, colloidal silica (from particles of SiO_2 dispersed in an organic solvent) is used for gelation Fine particles of SiO_2 are obtained by oxidation (in a flame, plasma or a heated tube) of its halide $SiCl_4$ Colloidal silica is prepared by dispersing SiO_2 particles in a non polar medium such as chloroform Shoup and Wein (1977) prepared the mixture of sodium or potassium metasilicate and colloidal silica sol (ludox) Formamide was added to it to control the pH and to promote gelation The gel was leached in weak acid to reduce the alkali content to less than 0 02 wt % Rabinovich et al (1982) and Johnson et al (1983) used 'fumed' silica to prepare silica gel This was a colloid produced by reacting silicon tetrachloride in a flame The colloidal particles were characterized by a particle size ~12nm and low impurity level The material was dispersed in a twice-deionized water using a blender to form a sol NH_4OH (58%) and HCl (density 1 19) were

used to adjust the pH of the sol Fluidity of the sol was found to be strongly

dependent on the pH On aging, the sol becomes gel Scherer and Luong (1984)

has also reported similar results using flame hydrolysed silica soot, dispersed in

a hydrophobic solvent

2.3.1 Chemistry of the Gel

Here elementary units of SiO_2 are dispersed in an aqueous

solvent This dispersed phase called 'sol' is then converted into a rigid

'gel' by destabilisation process (Scherer and Luong 1984) During

gelation, the overall medium becomes viscous and eventually solidifies

with the build-up of coherent network of praticles The schematic
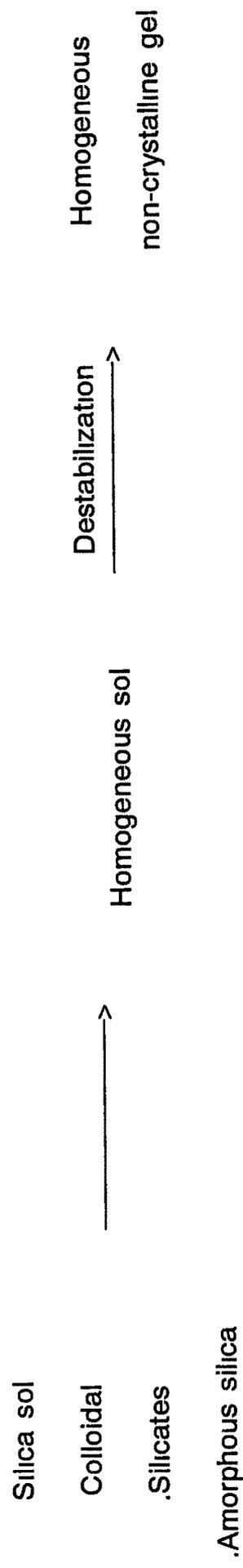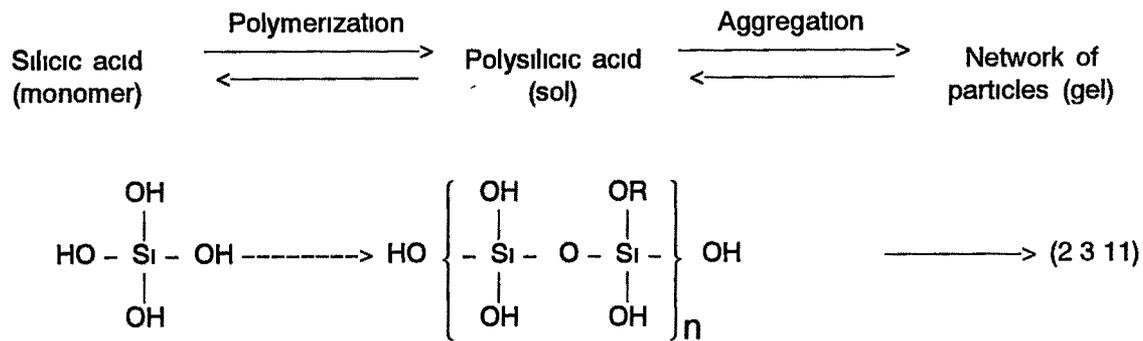
diagram of this process is shown in Fig 2 2

Silica sol
Colloidal
.Silicates
.Amorphous silica

⟶

Homogeneous sol

Destabilization ⟶

Homogeneous non-crystalline gel

Fig: 2.2 – Sol-Gel Process (Colloidal Method)

The gelling process of silica can be represented as follows

$$\text{Silicic acid (monomer)} \xrightleftharpoons[\text{}]{\text{Polymerization}} \text{Polysilicic acid (sol)} \xrightleftharpoons[\text{}]{\text{Aggregation}} \text{Network of particles (gel)}$$

$$
\underset{\underset{OH}{|}}{\overset{\overset{OH}{|}}{HO - Si - OH}} \xrightarrow{\hspace{1cm}} HO \left[\underset{\underset{OH}{|}}{\overset{\overset{OH}{|}}{- Si}} - O - \underset{\underset{OH}{|}}{\overset{\overset{OR}{|}}{Si -}} \right]_n OH \xrightarrow{\hspace{1cm}} (2\ 3\ 11)
$$

The gelling process consists of three stages

(i) formation primary particles (ii) growth of particles and linking of particles together into branched chains and (iii) formation of networks extending throughout the liquid medium thickening into gel The factors influencing the gelling process are the pH of the medium, the presence of a catalyst, particle size, its concentration in the medium and the temperature

2.3.2. Drying of the Gel

The conversion of a wet gel into a dry gel involves the removal of a large proportion of the remaining liquid phase (alcohol or water) During this stage, considerable shrinkage of the gel network occurs converting the soft gel progressively into a hard, porous solid (xerogel) The drying process is usually carried out at ambient or moderate temperature ($<100°C$) and must be performed extremely slowly over periods ranging from days to months to avoid cracking

and fragmentation (James 1988) It is generally accepted that the cracking arises from the capillary forces within the porous gel as the liquid evaporates Since these forces vary inversely with capillary (pore) size, cracking tends to be reduced if the pores are larger The problem of cracking in the case of gel prepared from colloidal method was solved by "double" processing (Rabinovich 1982) This process involves the usual preparation of sol by colloidal method The sol is dried by maintaining it at 150°C in an open beaker This results in the formation of dried fragments of porous silica This material is dispersed in the same manner as in the case of original starting material The new sol is gelled and dried at room temperature in air overnight or by heating it to 90°C to 110°C for about 10 hrs An uncracked porous silica is obtained

2.4 CONVERSION OF GEL INTO GLASS

A gel can be converted into glass in several ways (a) conversion of gel into glass at temperatures below the glass transition temperature T_g (b) conversion of gel into glass or glass-ceramic by sintering (with or without high pressure) at temperatures above T_g but well below the melting temperature (c) conversion of gel into glass by fusion (melting)

The first conversion route is based on the chemical polymerization process at low temperatures The process involves the removal of residual OH or OR groups by polycondensation reactions as represented by Example-1 of

section 2 2 1 With the further shrinkage in the volume, the pores in the gel gradually disappear The collapse and the elimination of pores is governed by the viscous flow, the driving force being supplied by the decrease in the surface energy of the porous gel The temperature at which the above process takes place depends on the size distribution of the residual pores in the gel The finer the pore size, the lower is the temperature During the heat treatment the departure of residual impurities such as water, organic residues and carbon may be accompanied by cracking Closure of pores may trap impurities which on forming glass, may expand to cause serious bloating of the sample Finally, the sintering process must be completed before significant crystallization of the gel takes place The kinetics of both sintering and crystallization increases with the rise in temperature and decreases with the increase in viscosity of the gel

Schroeder (1964) prepared thin glass films following this method The synthesis of glasses and glass-ceramics by hot pressing of gels has been reported by Dislich (1971), Mecarthy et al (1971), Decottignies et al (1977, 1978) The structure of the gel evolved progressively towards that of glass with the loss of water and porosity

The conversion of gel into glass below T_g has been investigated by several workers For example, Sakka and Kamiya (1978) reported that gel to glass transition starts above 800°C and the complete densification takes place around 1000°C Yamane et al (1979) studied the densification of silica gels prepared by the two methods mentioned above (sections 2 2 and 2 3) The

densification rate and the removal of organic groups was not the same in these cases The final densification took place at 1070°C Recently, Brinker and Mukherjee (1980) produced gels in a multicomponent system (SiO_2, B_2O_3, Al_2O_3, Na_2O, BaO) by two different methods and investigated gel to glass conversion They concluded that the densification rate and the removal of organic groups were dependent on the gel preparation procedures

Mukherjee et al (1976) had prepared multicomponent glasses by the fusion of gel after removing organic groups and water from it

In the case of non-silicate glasses, the conversion of gel to glass can be achieved at a temperature lower than that of silicate glasses For example, Tohge and Mackenzie (1984) had prepared $20Na_2O$-$80B_2O_3$ glass by heat treatment at 500°C for several hours

2.5 GENERAL FEATURES OF GLASSES PREPARED BY THE SOL-GEL METHOD

There are certain advantages of the sol-gel method of glass preparation as highlighted by some features of the sol-gel glass given below

1   High purity glasses can be prepared

2   Multicomponent glass and glass-ceramics of high homogeneity can be obtained

3   The glasses of compositions which could not be obtained by the conventional melting methods can be prepared by this method For example, the glass fibers of ZrO_2-SiO_2 system having 48% ZrO_2 were prepared by Kamiya et al (1980) by this method Preparation of this glass by melting method was found to be

unsuitable because it required extremely high temperature Further more one encounters difficult problems such as liquid immiscibility at the melting temperature, phase separation and crystallization during the cooling of the melt

4   Glasses and glass-ceramics can be obtained at relatively low temperatures

5   Final products can be obtained by simple operation without expensive facilities

6   In the sol gel glasses, structural variations in the polymer network can be affected without altering the composition These variations can be introduced by controlled hydrolysis - polymerization reactions of metal alkoxides On the other hand, in glasses prepared by conventional melt-quenching method, structural variations can be brought about only by compositional changes

2.6   THE PRESENT WORK

2.6.1 Starting Materials

In the present study, aqueous sodium metasilicate is used as the source of SiO_2 and Na_2O The gelification is brought about in the presence of acids like HCl Zinc oxide, phosphorous pentoxide, lithium sulphate and manganese sulphate have been added in small quantities to prepare ternary glass systems
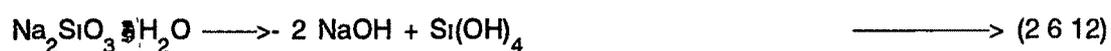
2.6.2 Gel Preparation

15ml of aqueous sodium metasilicate of specific gravity 1 39 was taken and 1ml of conc HCl was added to it at room temperature Here HCl acts as the catalyst The solution was stirred continuously for 10 to 15 minutes Transparent, colourless, low viscosity homogeneous
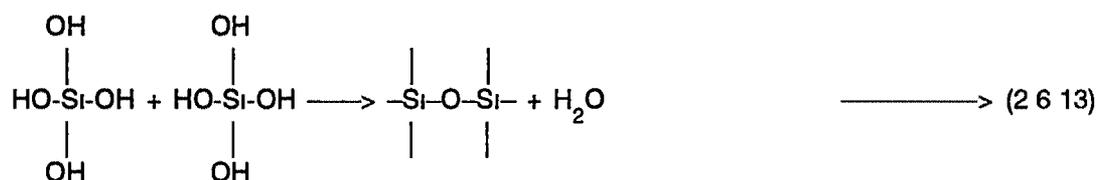
solution was thus obtained It was kept for gelling at room temperature
The gel was obtained in 3 to 5 days The reactions of gel formation
are represented as follows

Sample 1 :

Hydrolysis reaction:
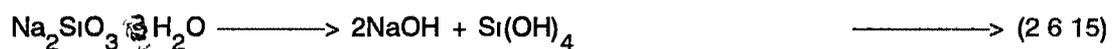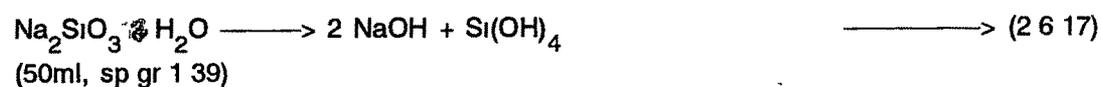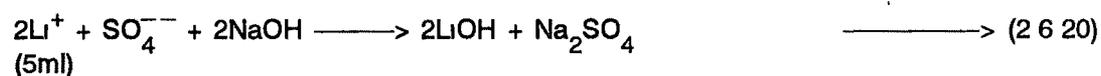
$$Na_2SiO_3 \cdot 9H_2O \longrightarrow 2\ NaOH + Si(OH)_4 \qquad\qquad \longrightarrow (2\ 6\ 12)$$

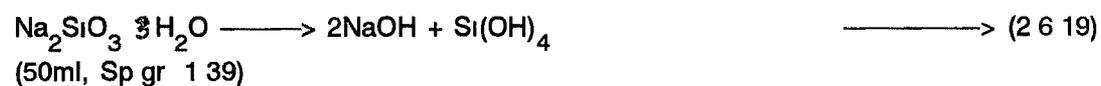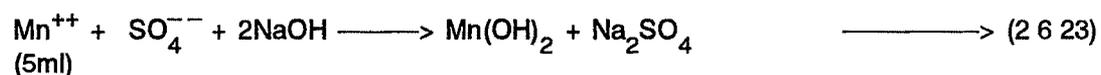### Polycondensation reaction:

$$\longrightarrow (2\ 6\ 13)$$

For the preparation of ternary glass a third component was
used as given in detail below

Sample 2 :

0 5gm of ZnO was dissolved in 5ml of HCl 5ml of this
solution was added to 45ml of aqueous sodium metasilicate of
specific gravity 1 40 The reactions of the gel formation can be
represented as follows

$$ZnO + 2HCl \longrightarrow ZnCl_2 + H_2O \qquad\qquad \longrightarrow (2\ 6\ 14)$$

$$Na_2SiO_3 \cdot 9H_2O \longrightarrow 2NaOH + Si(OH)_4 \qquad\qquad \longrightarrow (2\ 6\ 15)$$

Similarly, gels have been prepared using P_2O_5, Li_2SO_4 and
$MnSO_4$ respectively as the third component The reactions are as
follows

Sample - 3 :

$$P_2O_5 + 3H_2O \longrightarrow 2H_3PO_4 \qquad\qquad \longrightarrow (2\ 6\ 16)$$
(0 5gm) (5ml)

$$Na_2SiO_3 \cdot H_2O \longrightarrow 2\ NaOH + Si(OH)_4 \qquad\qquad \longrightarrow (2\ 6\ 17)$$
(50ml, sp gr 1 39)

Sample - 4 :

$$Li_2SO_4 \xrightarrow{H_2O(5ml)} 2Li^+ + SO_4^{--} \qquad\qquad \longrightarrow (2\ 6\ 18)$$
(0 5gm)

$$Na_2SiO_3 \cdot H_2O \longrightarrow 2NaOH + Si(OH)_4 \qquad\qquad \longrightarrow (2\ 6\ 19)$$
(50ml, Sp gr 1 39)

$$2Li^+ + SO_4^{--} + 2NaOH \longrightarrow 2LiOH + Na_2SO_4 \qquad\qquad \longrightarrow (2\ 6\ 20)$$
(5ml)

Sample - 5 :

$$MnSO_4 \xrightarrow{H_2O(5ml)} Mn^{++} + SO_4^{--} \qquad\qquad \longrightarrow (2\ 6\ 21)$$
(0 5gm)

$$Na_2SiO_3 \cdot H_2O \longrightarrow 2\ NaOH + Si(OH)_4 \qquad\qquad \longrightarrow (2\ 6\ 15)$$
(50ml, Sp gr 1 39)

$$Mn^{++} + SO_4^{--} + 2NaOH \longrightarrow Mn(OH)_2 + Na_2SO_4 \qquad\qquad \longrightarrow (2\ 6\ 23)$$
(5ml)
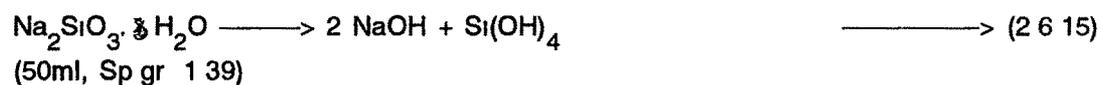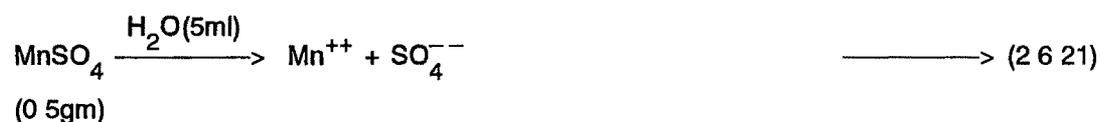
The gelation time can be reduced by using a catalyst For example, when P_2O_5 was used as one component, the time taken for gelation was 4 days Here P_2O_5 on dissolving with water becomes phosphoric acid which acts as the catalyst When ZnO was used as one component and conc HCl was used as the catalyst, gel was

formed in 3 days. In the case of Li_2SO_4 and $MnSO_4$ the gelation time was 7 days and 5 days respectively when no catalyst was used.

All the above gels were colourless and transparent except the gel containing $MnSO_4$ (which was pink due to Mn^{2+} ions)

2.6.3 Gel to Glass Conversion

A freshly prepared gel has large amount of liquid in it. Proper heat treatment is necessary to convert the gel into glass. Rapid heating causes the entrapment of gases in the gel body which leads to the formation of bubbles in the glass. Therefore the sample should be heated very slowly. The heat treatment results in the following simultaneous processes

(i) Condensation reaction (ii) transport and evaporation of reaction products (iii) pore shrinkage and closure. If these competing processes occur at a temperature where the resultant dense solid remains amorphous, the gel to glass transformation takes place. On the other hand, the process in which crystallization is not prevented, a polycrystalline glass-ceramic results
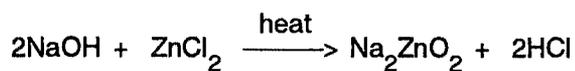
In the present work, the fusion method (section 2 4) is followed. The gels produced from the said procedure were dried at 50°C for about 10 days. Small bubbles have been observed due to the release of water. Further, the transparent gels became opaque

and porous when heated above 100°C. When the temperature reached around 700°C large shrinkage was observed with the elimination of pores The material softened around 850°C At 1100°C a clear, highly viscous fluid was obtained This melt was maintained at this temperature for one hour and the melt was quenched using splat quenching method (section 1 1 1) Glass samples obtained were transparent, colourless and non-hygroscopic whereas the glass containing Mn_3O_4 was dark violet in colour The reaction in gel to glass transition can be represented as follows
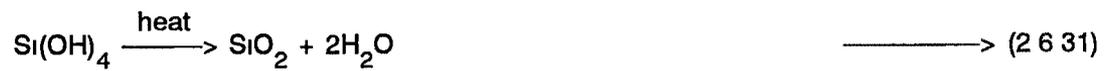
Binary Glass - Sample - 1 :

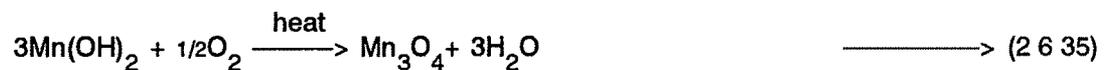$$2NaOH \xrightarrow{\text{heat}} 2Na_2O + H_2O \qquad\qquad\longrightarrow (2\ 6\ 24)$$

$$Si(OH)_4 \xrightarrow{\text{heat}} SiO_2 + 2H_2O \qquad\qquad\longrightarrow (2\ 6\ 25)$$

Ternary Glass - Sample - 2 :

$$Si(OH)_4 \xrightarrow{\text{heat}} SiO_2 + 2H_2O \qquad\qquad\longrightarrow (2\ 6\ 26)$$

$$2NaOH + ZnCl_2 \xrightarrow{\text{heat}} Na_2ZnO_2 + 2HCl$$

$$Na_2ZnO_2 \xrightarrow{\text{heat}} Na_2O + ZnO \qquad\qquad\longrightarrow (2\ 6\ 27)$$

Sample - 3 :

$$2H_3PO_4 \xrightarrow{\text{heat}} P_2O_5 + 3H_2O \qquad\qquad\longrightarrow (2\ 6\ 28)$$

$$2NaOH \xrightarrow{\text{heat}} Na_2O + H_2O \qquad\qquad\longrightarrow (2\ 6\ 29)$$

$$Si(OH)_4 \xrightarrow{\text{heat}} SiO_2 + 2H_2O \qquad\qquad\longrightarrow (2\ 6\ 30)$$

Sample - 4 :

$$Si(OH)_4 \xrightarrow{\text{heat}} SiO_2 + 2H_2O \qquad \longrightarrow (2\ 6\ 31)$$

$$2LiOH \xrightarrow{\text{heat}} Li_2O + H_2O \qquad \longrightarrow (2\ 6\ 32)$$

$$Na_2SO_4 \xrightarrow{\text{heat}} Na_2O + SO_2 + 1/2O_2 \qquad \longrightarrow (2\ 6\ 33)$$

Sample - 5 :

$$Si(OH)_4 \xrightarrow{\text{heat}} SiO_2 + 2H_2O \qquad \longrightarrow (2\ 6\ 34)$$

$$3Mn(OH)_2 + 1/2O_2 \xrightarrow{\text{heat}} Mn_3O_4 + 3H_2O \qquad \longrightarrow (2\ 6\ 35)$$

$$Na_2SO_4 \xrightarrow{\text{heat}} Na_2O + SO_2 + 1/2O_2 \qquad \longrightarrow (2\ 6\ 36)$$

Glass samples of different compositions have been prepared by changing the content of additives (1 2-7 0 (mole %)) It is noted that the preparation of glass from sodium metasilicate through the conventional method needs very high-temperature (>1200°C) On the other hand, sol-gel method needs the temperature below 1000°C

2.7 ANALYSIS OF THE GEL TO GLASS TRANSITION

The heat treatment process to form the glass from the gel was studied by differential thermal analysis (DTA) During the thermal treatment of gels several phenomena like dehydration, oxidation of the residual compounds, sintering, crystallization etc may occur In order to study the chemical structural changes in a given temperature range DTA, X-ray diffraction and IR transmission measurements are carried out

2.7.1. DTA

The thermograms of the gels frequently show significant drift of the base line and hence assignment of small intensity thermal effects is difficult

The DTA was carried out on different gels (derived at 80°C) from room temperature upto 700°C Heating rate was 20°C/min A static air atmosphere was maintained Al_2O_3 was used as the reference material Fig (2 3) shows the DTA trace of Na_2O-SiO_2-Li_2O gel It can be seen that around 70°C a small endothermic peak is observed which may be related to the release of water The presence of the exothermic peak around 520°C indicates gel to glass transition

2.7.2 X-ray Diffraction

X-ray diffraction analysis of all the glass samples have been done CuK_α radiation was used with a Ni filter Absence of crystalline peaks indicates the amorphous nature of their structure In the case of glass samples containing Mn_3O_4 crystalline peaks were observed when the composition of Mn_3O_4 was increased beyond 0 9% (mole%) The diffraction pattern of 33 3% Na_2O-66 7% SiO_2 glass is shown in fig 2 4

2.7.3 IR Transmission Spectroscopy

The samples were prepared using the KBr pellet technique The spectra were recorded in a double beam spectrometer (Perkin Elmer 580) The spectra of all the glass samples agree well with the
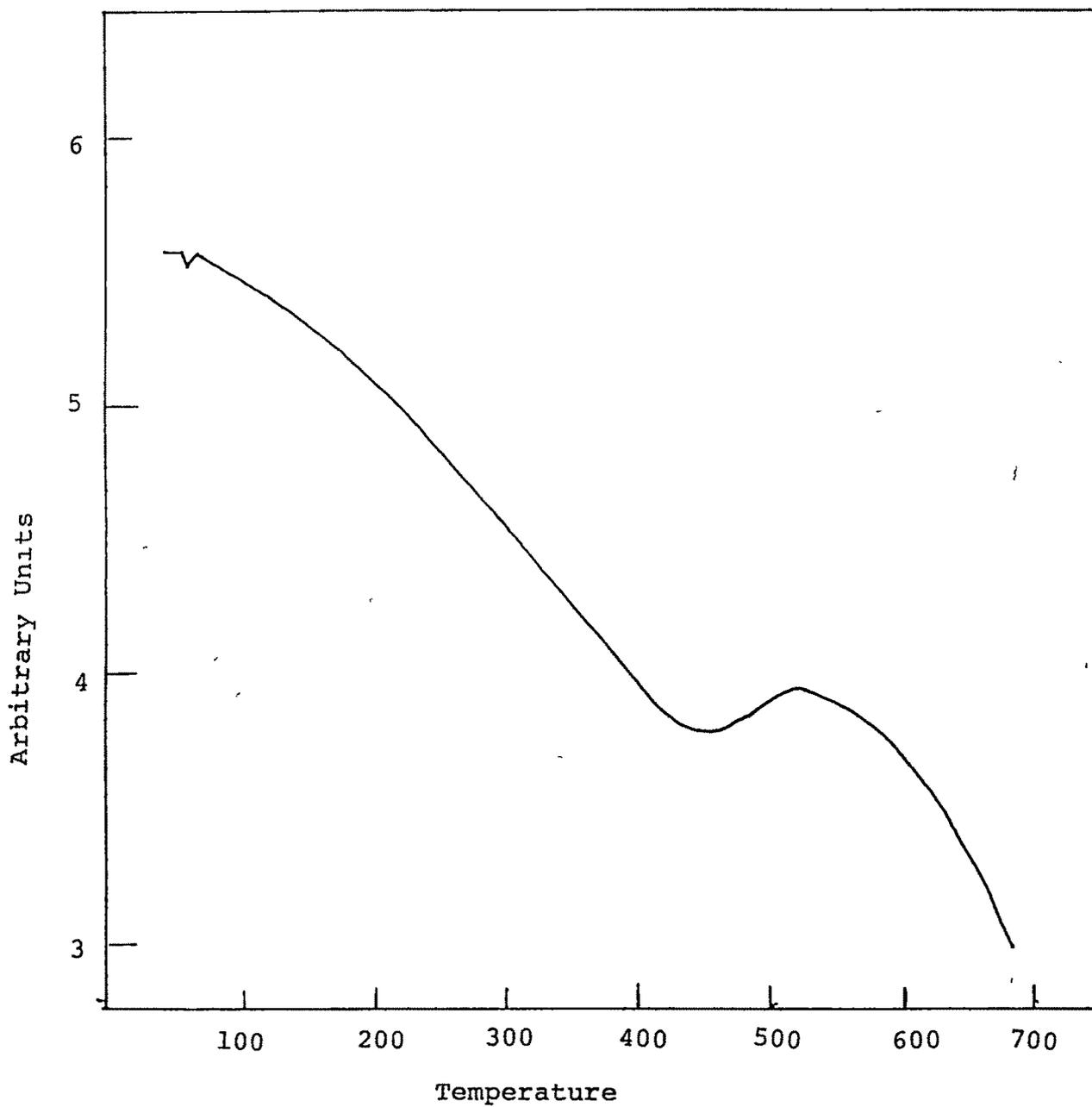
Fig. 2 3   DTA Trace of 26 9 Na$_2$O-71.6 SiO$_2$-1.5 Li$_2$O gel through gel-glass transition.
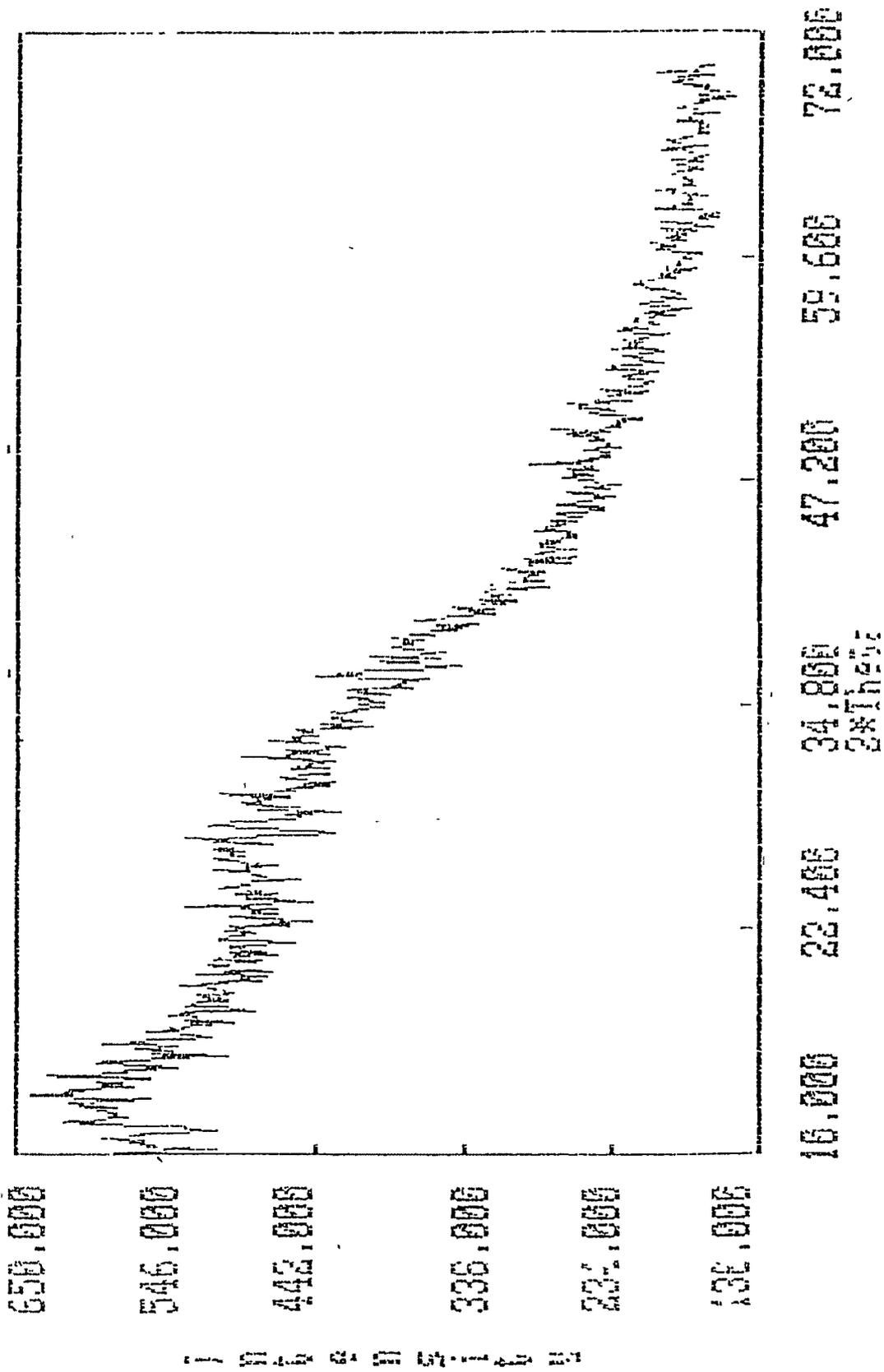
Fig. 2.4 : X-ray diffraction pattern of 27.1 Na_2O - 72 9 SiO_2 glass.

reported, spectra (See for example Prassas et al 1982, Hench et al 1982, Decottignies et al 1978) The spectrum of 27 1% Na_2O-72 9% SiO_2 glass is as shown the Fig 2 5. The band at 470cm^{-1} is attributed to the vibrational modes of deformation of the O-Si-O and Si-O-Si bonds The band at 770cm^{-1} is attributed to the ring structure of SiO_4 tetrahedra The large band at 1050cm^{-1} corresponds to the stretching vibration of the Si-O bond In addition to these characteristic bands, a very large band at 3450cm^{-1} is observed as a result of the superposition of vibration bands of hydroxyl groups and stretching vibrations of adsorbed water molecules

2.8 CONCLUSIONS

In the present work, sol-gel method has been used successfully for the preparation of binary and ternary silicate glasses using sodium metasilicate as the starting material The gel-glass transition and the amorphous nature of their structure were confirmed using the standard techniques like DTA, IR transmission and X-ray diffraction measurements Lower melting temperature and better homogeneity (because the mixing takes place in solution) are the main advantages of this method over the conventional method

However, in the present work there is limitation with respect to the variation in concentration of consituent elements For example, in the case of ternary glass Na_2O-SiO_2-ZnO the concentration of ZnO could be increased to 6 mole% only When the ZnO content was in creased further, homogeneous solution was not obtained
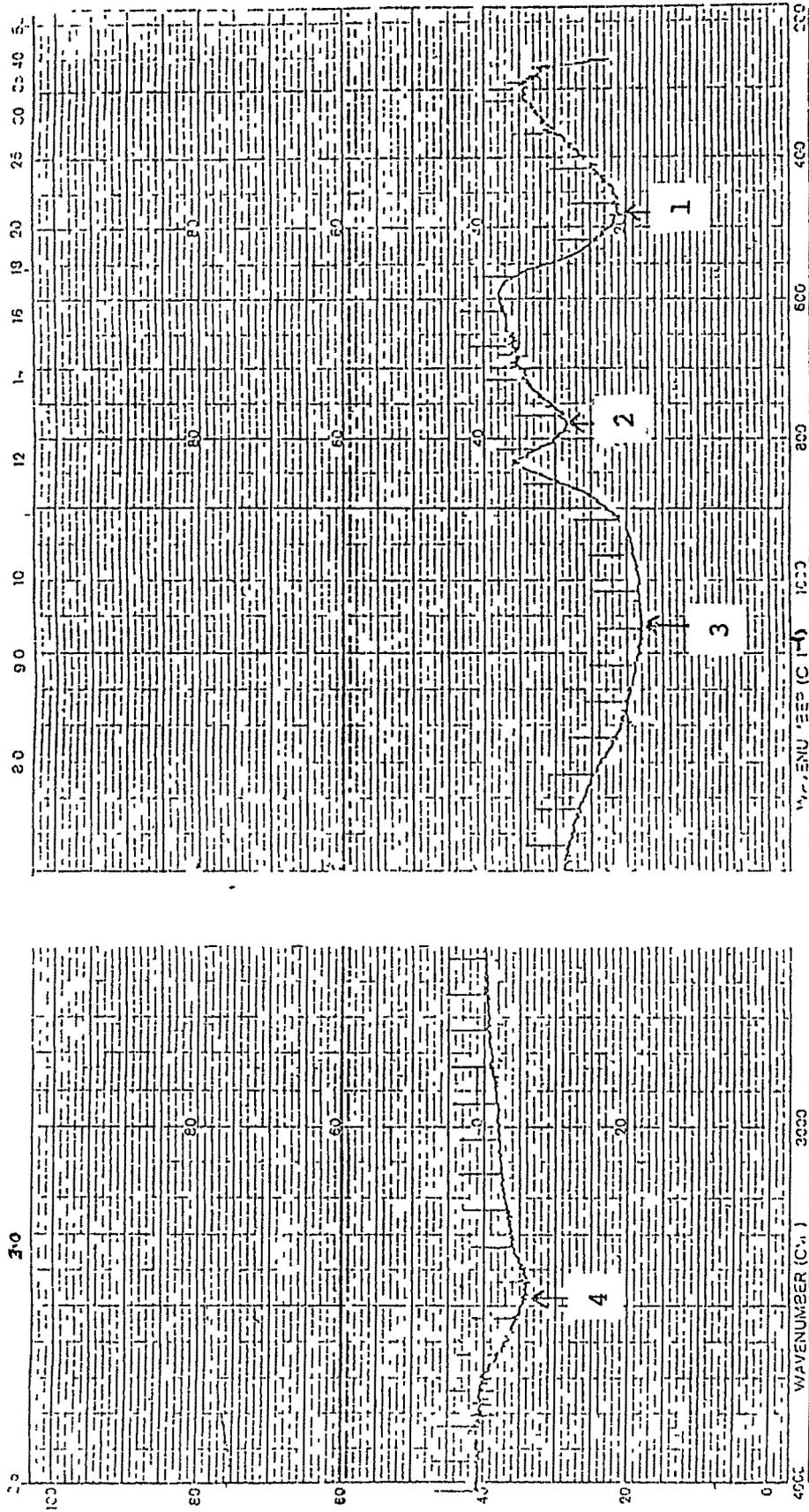
Fig 2.5 The infra-red spectrum of 27 1 Na_2O - 72.9 SiO_2 glass