JOURNAL OF MATERIALS SCIENCEA 28 (1993) 1097–1106

Novel low-temperature synthesis of glasses and glass-ceramics in the B_2O_3–SiO_2–P_2O_5 system

P.N. KUMTA, M.A. SRIRAM
Department of Materials Science and Engineering, Carnegie Mellon University, Pittsburgh, PA 15213, USA

In recent years considerable progress has been made in electronic packaging substrate technology. The future need of miniaturization of devices to increase the signal processing speed calls for an increase in the device density requiring the substrates to be designed for better thermal, mechanical and electrical efficiency. Fast signal propagation with minimum delay requires the substrate to possess very low dielectric constant. Several glasses and glass-ceramic materials have been identified over the years which show good promise as candidate substrate materials. Among these, borophosphate and borophosphosilicate glass-ceramics have been recently identified to have the lowest dielectric constant (3.8). Sol–gel processing has been used to synthesize borosilicate, borophosphosilicate and borophosphate glasses and glass-ceramics using inexpensive boron oxide and phosphorus pentoxide precursors. Preliminary results of the processing of these gels and the effect of volatility of boron alkoxide and its modification on the gel structure are described. X-ray diffraction, differential thermal analysis and Fourier transform-infrared spectroscopy have been used to characterize the as-as-prepared and heat-treated gels.

1. Introduction

The advancement and miniaturization of integrated circuits has made microelectronic packaging an integral part of device technology. The past four decades have witnessed a phenomenal growth and progress in semiconductor device technology that has placed stringent requirements on microelectronic packaging especially in the area of electronic substrates. The substrates need to possess good mechanical, thermal and electrical properties in order to satisfy the strength, heat dissipation and fast signal propagation criteria. Ceramic packaging is one of the most active areas in packaging and the role of ceramic materials as substrates in several packages such as dual-in-line packages, chip carriers, and pin grid arrays, is well known [1–6]. This is because ceramics possess a combination of electrical, thermal, mechanical and dimensional properties that are far superior to any other group of materials, including metals and plastics.

1.1. High thermal conductivity ceramics

Ceramics have dielectric constants spanning 4–10 000, thermal expansion coefficients matching silicon ($30 \times 10^{-7}\,^{\circ}C^{-1}$), and a range of thermal conductivities making them one of the best materials for insulation to heat conduction better than aluminium metal. They are also highly refractory with excellent temperature stability making them good materials for hermetic applications. The main drawback of ceramic materials is the fact that they are brittle and require very high processing temperatures. Research in the development of materials for packaging application has been focused at achieving objectives which include lower dielectric constant, lower processing temperatures, good thermal expansion match with silicon, improved thermal conductivity, efficient and reliable techniques of power dissipation, multilayer processing and high mechanical strength. Table I lists the ideal properties of a ceramic package. A number of ceramic materials have been developed and are being actively researched into, so that packages will have improved (1) signal propagation, (2) thermal expansion matching that of silicon and allowing larger chips of high circuit density to be directly solder-bonded, (3) electrical conductors for enhanced power distribution, (4) thermal conductors for improved power dissipation, and (5) input/output connection to support more circuits. The materials that have been identified for these purposes are AlN, BeO, SiC, cubic BN and diamond among the ceramic materials, while glasses and glass-ceramics have also been investigated for packaging applications because of their low dielectric constants. Table II lists the relevant properties of these materials [1, 7].

1.2. Glass-ceramics

Glass-ceramics have a dielectric constant around 5 and an excellent thermal expansion match with silicon. This, coupled with the ability to co-sinter with copper, or gold, makes them potentially one of the best candidate materials for high-performance multilayer ceramic substrates. In addition, their surface properties make thin-film metallization and deposition of dielectric materials very easy making them an excellent choice for high-performance application. The major disadvantage of glass-ceramics is their low thermal conductivity which makes them poor materials for heat dissipation in packaging application where the chip is bonded facein-in-the-cavity-up configuration. However, in those applications where the heat dissipation occurs from the back of the chip, this limitation is largely overcome by external routes and a water cooling mechanism, as in the thermal conduction module of IBM [8]. In this case, much of the heat is removed by the external cooling modes rather than the substrate itself and hence glass-ceramics with lower dielectric constants serve as better materials than the other covalently bonded ceramics listed in Table II. The low dielectric values of glass-ceramics have attracted considerable research in this class of materials. Table III lists several glass, glass-ceramic, and combination of glasses added to various ceramics along with their dielectric values.

2. Potential glasses and glass-ceramics

From several materials listed in Table III, cordierite, borosilicate glasses, and glass-ceramics of these two systems have received the most attention. Recently, MacDowell and Beall [9, 10] reported on the synthesis of glass-ceramics in the borophosphosilicate system. They reported the crystallization of BPO_4 from a silica-based glass using conventional melt-quenching techniques.

2.1 Borosilicate glasses

Borosilicate glasses exhibit a dielectric constant of 4 and have been identified to be one of the major constituents in glasses and glass-ceramics for future high-performance ceramic packaging applications [1, 7]. Prior to finding its use in electronic packaging, there were several reports regarding the application of the sol–gel technique for the processing of borosilicate glasses [11–22]. Since the development and identification of glass-ceramics as promising materials for high performance packaging applications, there has been a great deal of interest in the processing and electrical properties of borosilicate glasses and composites of borosilicate glass and crystalline ceramics. Niwa *et al.* [23, 24] have reported studies on composites of boro-

TABLE I Ideal properties of ceramic packaging

Dielectric constant	≤ 5
Coefficient of thermal expansion	$30 \times 10^{-7}\,°C^{-1}$
Package metallization	
Resistivity	2 μΩ cm
Metallization layers	
Thick film	$\leq$ 75 μm on 500 μm up to 100 layers
Thin film	$\leq$ 25 μm on 75 μm, up to 10 layers
Number of contacts to chip	up to 1000 per chip site
Number of package output pins	$> 20\ cm^{-2}$

TABLE II Properties of selected ceramic substrate materials

Substrate properties	AlN	SiC	BeO	Glass-ceramics	90% alumina	Cubic BN	Diamond
Thermal conductivity ($Wm^{-1}K^{-1}$)	230	270	290	5	25	250	2000
Coefficient of thermal expansion (20–200 °C) ($10^{-7}\,°C^{-1}$)	43	37	68	30–42	67	48	35
Dielectric constant at 1 MHz	8.9	42	6.8	5.0	9.4	7.1	5.6
Flexural strength (MPa)	350	420	250	210	280	–	–

TABLE III Properties of glasses, glass + ceramics, and glass-ceramics

Materials	Dielectric constant	Coefficient of thermal expansion ($10^{-7}\,°C^{-1}$)
Glasses		
B_2O_3–SiO_2–Al_2O_3–Na_2O	4.1	32
Glass + ceramics		
$PbO + B_2O_3 + SiO_2 + (Al_2O_3)$	7.5	42
$MgO + Al_2O_3 + SiO_2 + B_2O_3 + (Al_2O_3)$	4.5	30
$B_2O_3 + SiO_2 + (Al_2O_3)$	5.6	45
$2MgO.2Al_2O_3.5SiO_2 + (Al_2O_3)$	5.5	30
$CaO + Al_2O_3 + SiO_2 + B_2O_3 + (Al_2O_3)$	7.7	55
$Li_2O + SiO_2 + MgO + Al_2O_3 + SiO_2 + (Al_2O_3)$	7.3	59
$Li_2O + Al_2O_3 + SiO_2 + (Al_2O_3)$	7.8	30
Glass-ceramics		
MgO–Al_2O_3–SiO_2–B_2O_3–P_2O_5	5.0	30
Li_2O–Al_2O_3–SiO_2–B_2O_3	6.5	25

silicate glass and crystalline quartz, cordierite and mullite. Similarly, Kata *et al.* [21] have reported studies on electrical properties of glass-ceramics of borosilicate glass (BSG) containing quartz. They also studied composites of borosilicate glass with cordierite as well as borosilicate glass containing quartz and cordierite. Their studies indicate that the combination of borosilicate glass and quartz has an extremely low dielectric constant of 4.1, and with the introduction of some porosity, the dielectric constant can be lowered to a value as low as 3.9. The composites containing quartz and cordierite, however, have a higher dielectric constant of 4.7. In any case, it has always been shown that glass-ceramics and glasses are good candidate materials for electronic packaging exhibiting low dielectric constants. The thermal conductivity of these materials is however, very low, making them suitable for flip chip device technology where the bulk of the heat is removed from the rear of the die. The thermal conductivity of the substrate therefore, does not make a major difference [7].

2.2 Borophosphosilicate glasses

Borophosphosilicate glasses had been synthesized by Zarzycki *et al.* [18] using the sol–gel process and recently Chou [25] reported the sol–gel synthesis of monolithic bulk glasses of borophosphosilicate glasses. Their work demonstrates the application of the sol–gel process for synthesis of multicomponent glasses; however, MacDowell and Beall in 1989 [9, 10] showed the potential of these glasses for electronic packaging. MacDowell and Beall have shown that glasses in the B_2O_3–P_2O_5–SiO_2 system having individual components in the molar ratio of 1:1:1 and 1:1:3, are not very chemically resistant against water, acids and bases. However, they have reported that crystalline boron phosphate (BPO_4) can be internally nucleated from these glasses resulting in a very durable glass-ceramic with the residual glass being rich in SiO_2. The thermal expansivity of the boron phosphate glass-ceramic according to their reports is low to moderate between 4.5 and $5.5 \times 10^{-7}\,°C^{-1}$ but their unique feature is their low dielectric value of 3.8–4.5 and the loss tangents which are below 10^{-3} above 1 kHz and up to 200 °C.

2.3 Sol–gel synthesis

The sol–gel process consists of the use of metal alkoxide precursors which are hydrolysed in a controlled manner with the use of suitable catalysts to obtain oxide gels, monolithic glasses, ultrafine powders and thin films. The controlled hydrolysis is followed by polymerization and condensation reactions resulting in the formation of corresponding metal oxides [26]. The technique and methodology was probably first applied for making synthetic clays by Ewell and Insley [27] in 1935 but its applicability for the preparation of ceramics was first demonstrated by Roy [28–31]. Roy exploited this route for synthesizing a wide range of ceramic materials and was responsible for introduction of the term "sol–gel". The technique is extremely powerful and versatile and has several advantages: (1) The use of this technique results in the formation of high-purity ceramics because of the use of organometallic precursors that can be obtained in a very pure state by repeated fractional distillation. (2) The use of catalysts can control the rate of hydrolysis and the subsequent polycondensation reactions to result in the formation of either monolithic glasses, ultrafine particles or thin films. (3) The hydrolysis reactions can be controlled to tailor the composition in the ultimate ceramic to the desired specifications. The resultant gels and precipitated particles are extremely fine with specific surface areas in excess of 200 m^2gm^{-1} which make the particles very reactive, leading to considerable reduction in the sintering temperatures [32–39].

Sol–gel processing of borosilicate and borophosphosilicate glasses has always consisted of using boron alkoxide or trialkyl borate, $B(OR)_3$, and tetraethoxyorthosilicate (TEOS) in the case of borosilicate glasses or trialkyl borate, $B(OR)_3$, trialkyl phosphates $(RO)_3PO$, trialkyl phosphites $(RO)_3P$ and TEOS for synthesis of borophosphosilicate glasses, where R represents methyl and ethyl groups. All these metallorganic precursors are extremely moisture sensitive and susceptible to rapid hydrolysis on exposure to moisture. The instability of phosphorous and boron alkoxides in contrast to silicon (TEOS) leads to significant differences in the hydrolysis rates of the different precursors resulting in chemically inhomogeneous gels. There is, therefore, considerable research being focused on modification of the alkoxide precursors to control the hydrolysis rates of various molecular species to obtain ceramics and gels of uniform composition [40, 41]. The modification is achieved by complexing the metal alkoxides by use of modifiers such as acetic acid and acetyl acetonate (acac). This results in a reduction in the number of alkoxy (OR) groups available for hydrolysis. There have also been some studies on the use of other precursors to counteract this problem. Chou *et al.* [25] recently reported the use of boric acid as an alternative precursor instead of the alkoxide to synthesize borophosphosilicate monolithic gels. In the present paper, we describe an inexpensive modified sol–gel processing route utilizing the oxides, B_2O_3 and P_2O_5 as precursors for synthesis of borosilicate, borophosphosilicate and borophosphate gels. The route involves *in situ* preparation of the alkoxides in solution and a study of the effects of processing conditions and the possible chemical modification of boron precursors on the resultant gel compositions.

3. Experimental procedure

Three different gel systems were investigated, namely, borosilicate, borophosphosilicate and borophosphate. The procedures for the preparation of these gels are described below.

3.1 Borosilicate glasses

These glasses were prepared using boron oxide as precursors, while *in situ* modification of the alkoxide using acetyl acetonate (acac-H) was also attempted. A typical procedure for synthesis of these glasses consists of preparation of a clear solution of boron oxide in an acidified alcohol solution to which TEOS was added. Three compositions were selected corresponding to B_2O_3/SiO_2 ratios of 1:1, 1:2 and 1:4. The solution mixture was stirred to obtain a clear sol. Two-stage water additions were used. The first addition was accompanied by heating the mixture to 60–70 °C followed by a second-stage addition of slightly basic deionized water. The clear solution was then allowed to gel by covering the beakers with a parafilm seal. Initiation of gelation occurred within 24 h, while complete drying of the gels was achieved in 7 days. In all the gels an *r* ratio of 12 was maintained. The air-dried gels were then heated to 150 °C for approximately 48 h. Fig. 1 shows the flow sheet for the synthesis of these gels. The modified gel process using acacH was synthesized in a similar manner by dissolving B_2O_3 in an acidified alcohol solution and adding acacH to the clear solution. A prehydrolysed solution of TEOS containing alcohol and water was then added to the solution containing boron. The two sols were mixed at approximately 50°C, after which a basic deionized water solution was added (see Fig. 2). The solution was allowed to gel at 50 °C, after covering the beaker with parafilm.

3.2 Borophosphosilicate glasses

Two compositions were selected containing $B_2O_3:P_2O_5:SiO_2$ in the ratio of 1:1:4 and 1:1:8. Once again a similar procedure was followed. The

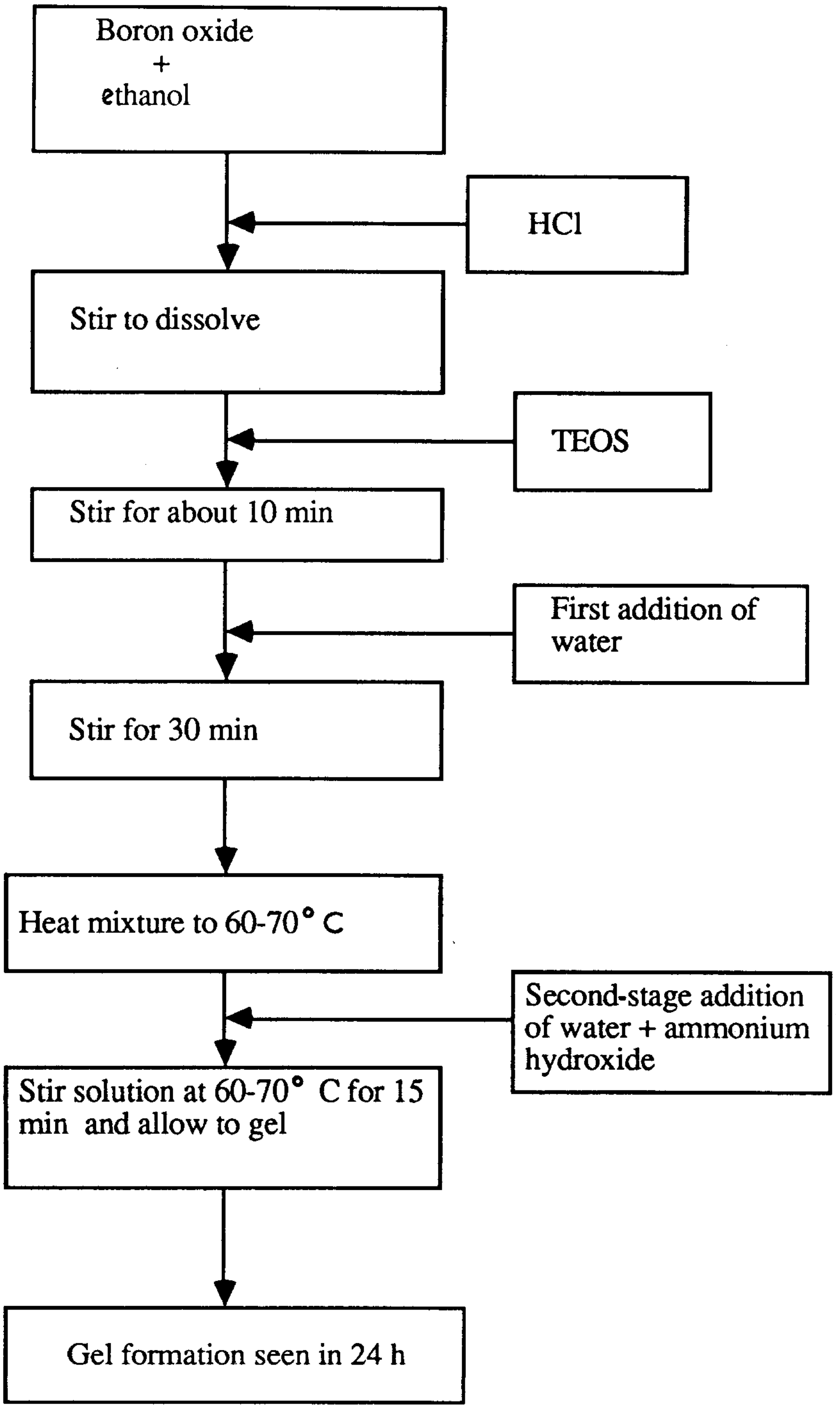

Figure 1 Flow sheet showing the scheme for synthesizing borosilicate gels.

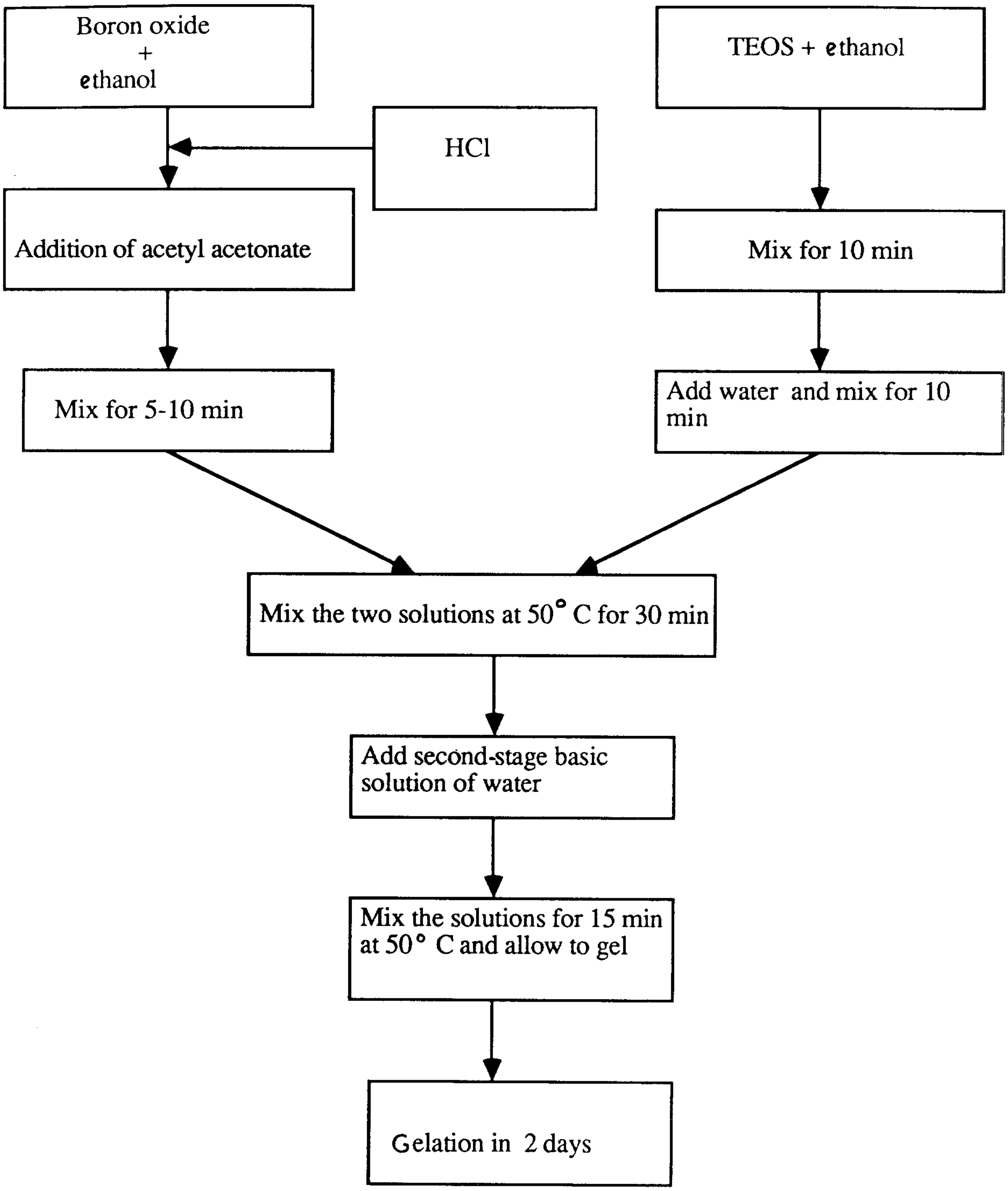

Figure 2 Flow sheet showing the synthesis of borosilicate gels with acetylacetonate modification.

stoichiometric amounts of B_2O_3 and P_2O_5 were dissolved in an acidified solution of alcohol to which TEOS was added. The hydrolysis was initiated by following a two-step procedure. The initial amount of water was added after the introduction of TEOS. The solution was mixed at 60 °C for 2 h after which the remaining amount of water in the form of a basic solution was added. The solutions were mixed at 60 °C and the beaker was then sealed by parafilm and allowed to gel. Gelation was achieved in 5 days. An r ratio of 27 and the alcohol to TEOS (e ratio) of 20 was used for both the compositions. The air-dried gels were then heated at 150 °C for 48 h and then subsequently heat treated at 450 ° and 650 °C for 12 h at each of these temperatures. Fig. 3 shows the schematic diagram of the procedure described above.

3.3. Borophosphate gels

These gels were prepared once again from boron oxide and phosphorous pentoxide as shown in Fig. 4. Stoichiometric amounts in the ratio of 1:1 were dissolved in an acidified alcohol solution. The mixture was stirred at room temperature for 5–6 h in a beaker provided with a parafilm seal. Deionized water was then added and the mixture stirred for approximately 8 h until the solution became increasingly viscous. The viscous solution was poured into a petridish and heated to approximately 70 °C until it transformed to a dry gel. The dried gels were then heated at 150 °C for 24 h and analysed using X-ray diffraction.

The glasses and gels in the three systems above were characterized using X-ray diffraction (XRD), Fourier transform-infrared spectroscopy (FTIR) and differ-

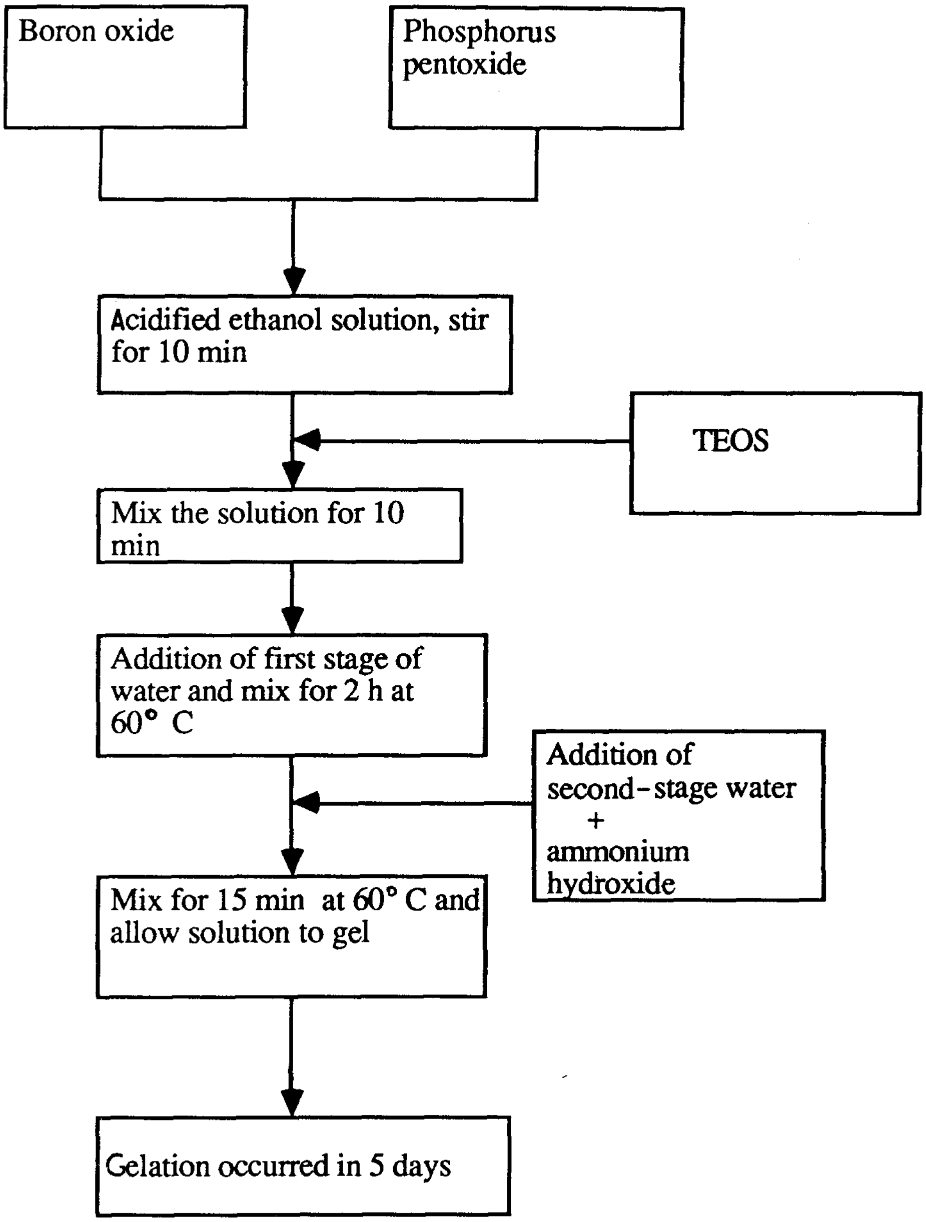

Figure 3 Flow sheet showing the scheme for synthesizing borophosphosilicate gels.

ential thermal analyses (DTA). Differential thermal analyses was performed on a Perkin–Elmer unit capable of monitoring the temperature upto 1000 °C. Preliminary FTIR scans were collected in the spectral range 400–4000 cm^{-1} using NaCl windows (spectral range 4000–6000 cm^{-1}) for the liquid samples on a Nicolet DX instrument. The dried gels were scanned in the wavelength range using the KBr pellets method.

4. Results and discussion

The results of the experiments performed in this work will be discussed separately for the three different glass systems. The paper represents the preliminary experiments performed to synthesize glasses in these three systems using an inexpensive and relatively easy procedure without involving the need for strict atmospheric control. The results indicate that the processing conditions play a very critical role in the generation of clear and homogeneous gels. In the three different systems discussed in this paper, it will be shown that the nature of addition of the precursors and the extent of contact with moisture during subsequent processing steps all seem to play an important role on the nature, morphology, crystallinity and phase evolution during heat treatment of the gels.

4.1. Borosilicate gels

Three compositions of the gels were prepared corresponding to different amounts of B_2O_3. The gels were synthesized according to the procedure described, in which B_2O_3 was dissolved in anhydrous 200 proof alcohol. Boron oxide went into solution in about 10 min. The oxide dissolves in the acidified alcohol solution to form the corresponding alkoxide according to the following reaction [42]

$$B_2O_3 + 6C_2H_5OH \rightarrow 2B(OC_2H_5)_3 + 3H_2O \qquad (1a)$$

$$B_2O_3 + (6 - 2n)C_2H_5OH \rightarrow 2B(OH)_n(OC_2H_5)_{3-n} + (3 - 2n)H_2O \qquad n = 0 - 3 \qquad (1b)$$

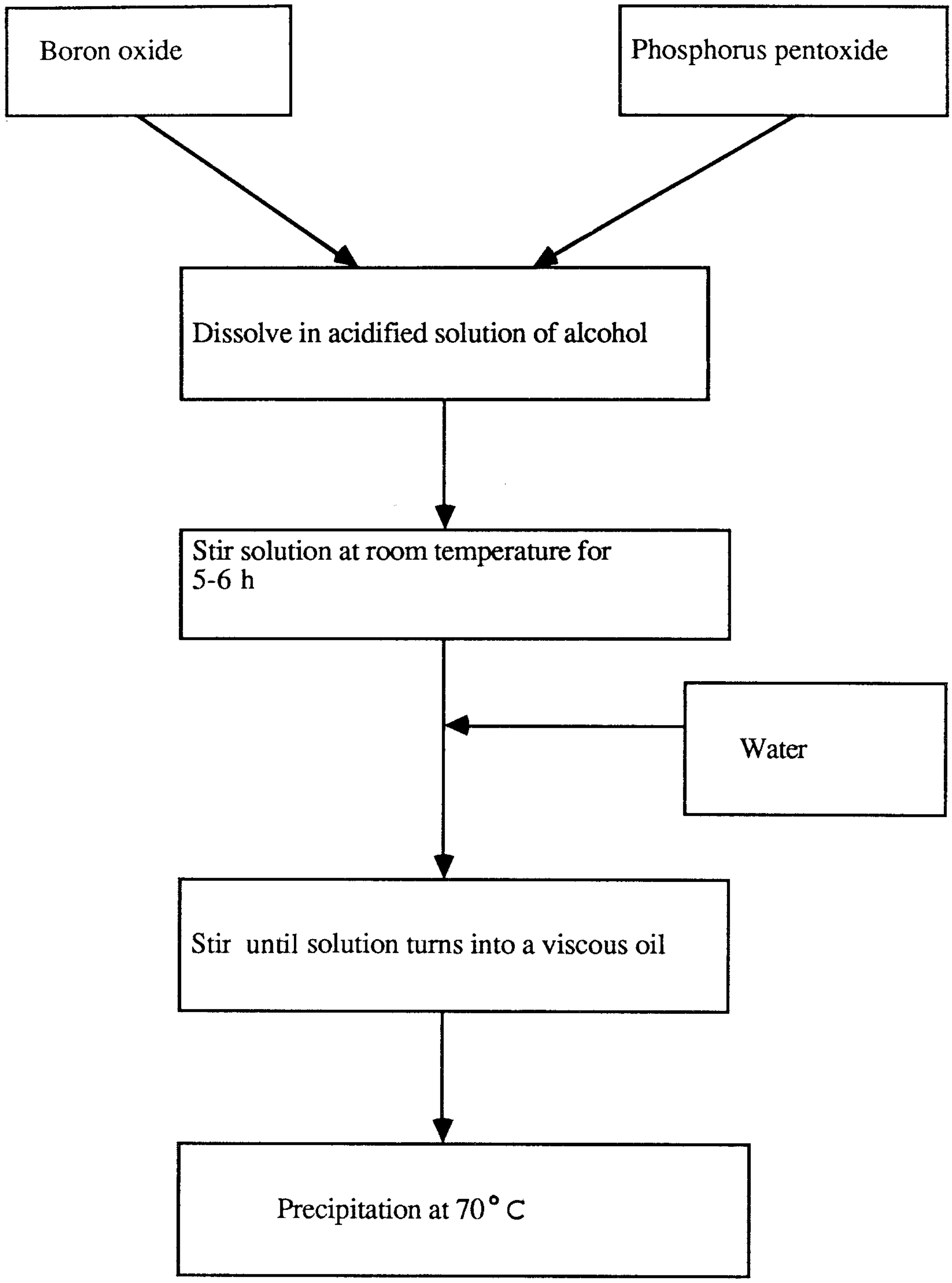

Figure 4 Flow sheet showing the scheme followed for generating borophosphate gels.

The formation of the alkoxide also results in the release of corresponding amounts of water which helps in the prehydrolysis reaction of TEOS. The alkoxide formed however, is extremely unstable and reacts with water almost instantaneously. The intensity of the reaction can be seen by the formation of a white residue on the walls of the beaker during stirring. The *in situ*-prepared alkoxide then reacts with TEOS to form borosiloxane chains as follows

$$\begin{aligned}&B(OH)_n(OC_2H_5)_{3-n} + Si(OH)_m(OC_2H_5)_{4-m}\\&\rightarrow (OH)_{n-1}(OC_2H_5)_{3-n}B\text{–}O\text{–}Si(OC_2H_5)_{4-m}(OH)_{m-1}\\&\quad + H_2O\\&\rightarrow (OH)_n(OC_2H_5)_{2-n}B\text{–}O\text{–}Si(OC_2H_5)_{4-m}(OH)_{m-1}\\&\quad + C_2H_5OH \qquad n = 0 - 3,\ m = 0 - 4 \qquad (2)\end{aligned}$$

The borosiloxy compound then is attacked by water to undergo hydrolysis and condensation to form terminal borosiloxy bonds. The reaction of the *in situ* generated boron alkoxide with TOES, however, should occur very quickly in the absence of water, or else premature hydrolysis of the boron alkoxide could occur leading to the precipitation of boron oxide trapped in the gel network. Fig. 5 shows the XRD trace of the borosilicate gel dried at 150 °C. The X-ray trace indicates the presence of B_2O_3 which could be occurring because of the hydrolysis of boron alkoxide before its reaction with TEOS. However, not all the boron alkoxide is lost as boron oxide because the infrared spectra collected on these gels show the absorption peak at 670 cm^{-1} corresponding to borosiloxy chains [43] (Fig. 6). DTA performed on the gel samples showed broad endothermic peaks corresponding to the loss of organics and water.

Based on these results it could be analysed that the source of crystallization of B_2O_3 could be as follows: (1) premature hydrolysis of boron alkoxide prior to reaction with TEOS, (2) hydrolysis of borosiloxy chains by water causing redissolution of borosiloxy networks and precipitation of B_2O_3, (3) boron diffuses to the surface during drying and reacts with atmospheric moisture to form boric acid that transforms to B_2O_3 during heat treatment at 150 °C. The *in situ* generated boron alkoxide is, therefore, very moisture sensitive leading to the formation of crystalline B_2O_3. The effect of crystalline B_2O_3 on the dielectric properties of the glass is currently being assessed. In the light of these results, efforts were directed towards the use of modifying agents such as acetylacetonate to modify the highly reactive boron alkoxide precursors.

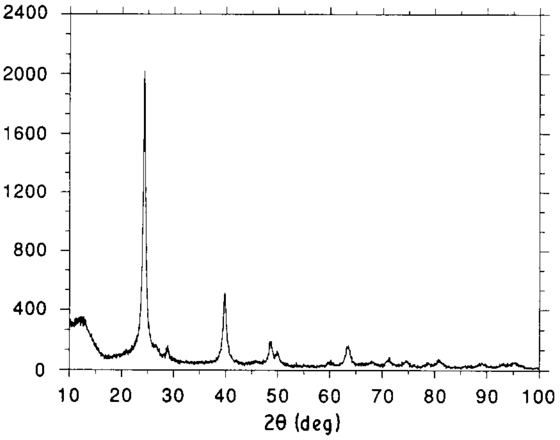

Figure 5 X-ray diffraction trace of borosilicate gels dried at 150 °C showing the presence of crystalline B_2O_3.

4.1.1. Acetylacetonate modification of borosilicate gels

The modification reactions of acetylacetonate have been well reported in the literature, particularly for group III alkoxides such as aluminium and the other group elements particularly, titanium and zirconium. The stabilization is achieved by the reaction of the alkoxide with the acetylacetonate molecules forming a stable chelate as follows:

$$B(OC_2H_5)_3 + acacH \longrightarrow B(OC_2H_5)_2(acac) + C_2H_5OH \qquad (3)$$

The formation of the metal chelate with acacH tends to stabilize the alkoxide against preferential rapid hydrolysis and substitution reactions [44]. Indeed, these modifications do occur, because the modified gels on heat treatment under identical conditions do not show the presence of any crystalline B_2O_3 as seen in the X-ray diffraction earlier (Fig. 7). These results are very promising and additional work is currently under progress to understand the modification reaction and the difference in the structure of the gels with and without modification.

4.2. Borophosphosilicate gels

The gels in this system were prepared in an analogous manner using boron oxide and phosphorus pentoxide under similar preparatory conditions. The as-prepared gels dried at 150 °C for 48 h were X-ray amorphous (Fig. 8) contrary to those cases reported by Zarzycki [37] in which BPO_4 crystallites were seen in the as-prepared gels. The DTA analyses also failed to show any crystallization peaks for both the composition studied, namely B_2O_3–P_2O_5–SiO_2 (1:1:4 and 1:1:8). The gels were further heat treated to

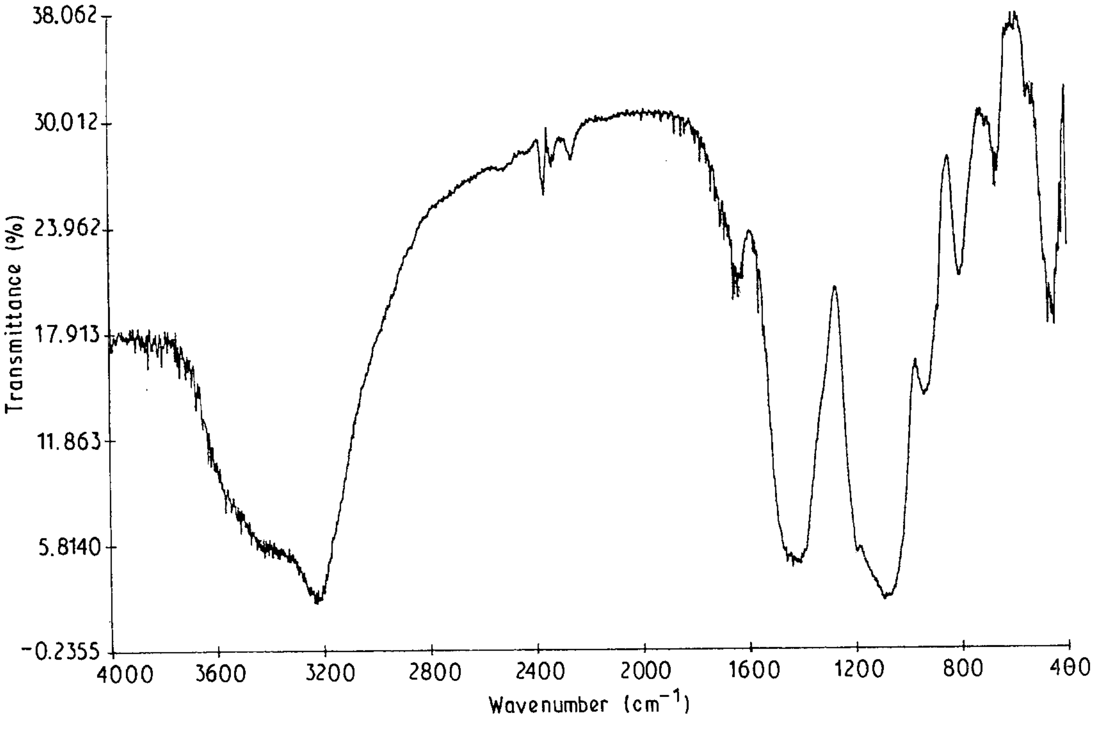

Figure 6 Infrared spectra of borosilicate gels indicating the presence of borosiloxy linkage at 670 and 930 cm^{-1}. Other linkages correspond to Si–O at 870 and 1089 cm^{-1}, $SiOC_2H_5$ at 1195 cm^{-1}, B–O bonds at 1400 cm^{-1} and molecular water at 1630 cm^{-1} [43].

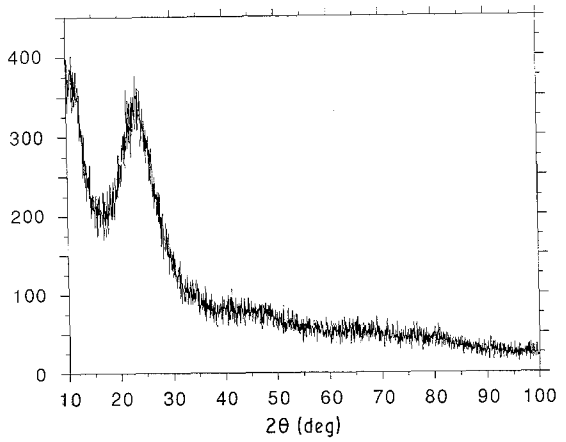

Figure 7 X-ray diffraction trace of acacH modified borosilicate gels showing the absence of crystalline boron oxide.

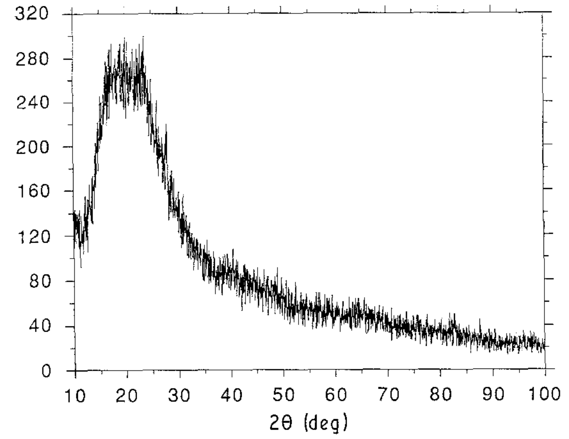

Figure 8 X-ray diffraction trace of amorphous as-prepared borophosphosilicate gels.

450 °C and 650 °C and held for 12 h at each of the temperatures. Fig. 9 shows the XRD trace obtained for the synthesized gels. The slow kinetics of the crystallization is evident from the low intensity of the peaks, which correspond to crystalline boron orthophosphate (BPO_4), and $3SiO_2 \cdot 2P_2O_5$. The emergence of these two phases is clearly an indication of the effect of processing condition on the gel formation similar to that seen in the preparation of borosilicate gels. The compositions selected were identical to those reported by MacDowell and Beall [9, 10]. Their reports indicate the formation of internally nucleated BPO_4. The formation of silicon phosphate in the present experiments could be explained on the basis that although the starting composition was selected to correspond to formation of BPO_4, there is loss of boron due to the volatile nature of boron alkoxide. As both boron oxide (B_2O_3) and phosphorus pentoxide (P_2O_5) are extremely hygroscopic, exact stoichiometry could not be maintained. Thus, one could expect the deviation in stoichiometry due to the presence of excess P_2O_5 resulting in the formation of the two phases. The presence of moisture, therefore, plays a deleterious role on homogeneous gel formation. However, the use of acacH modification, similar to the case of borosilicate gels could result in slowing down the hydrolysis of boron alkoxide and thereby result in a homogeneous gel. These observations are currently being examined in a systematic manner.

4.3. Borophosphate gels

Borophosphate gels were prepared by dissolving stoichiometric amounts of B_2O_3 and P_2O_5 in acidified solution of alcohol. The oxides were dissolved in water to which was added excess deionized water at 70 °C to initiate the precipitation of borophosphate. XRD of the precipitate dried at 150 °C for 24 h showed the formation of crystalline BPO_4 (Fig. 10). An interesting observation is the fact that there is no presence of crystalline boron oxide. We are currently in the process of investigating the reaction in detail, and hence at this point we can hypothesize that the dissolution of B_2O_3 and P_2O_5 results in the formation of the alkoxides of boron and phosphorus. Continued reaction of the two species further could result in condensation of the reactive alkoxy groups to form a borophosphate bond as follows

$$\begin{gathered}B(OR)_{3-m}(OH)_m + P(O)(OR)_{3-n}(OH)_n \rightarrow \\ (OH)_{m-1}(OR)_{3-m}\text{-}O\text{-}P(O)(OR)_{3-n}(OH)_{n-1} + H_2O \end{gathered} \quad (4a)$$

or

$$\begin{gathered}B(OR)_{3-m}(OH)_m + P(OR)_{3-n}(OH)_n \rightarrow \\ (OH)_{m-1}(OR)_{3-n}B\text{-}O\text{-}P(OR)_{3-n}(OH)_{n-1} + H_2O \\ R = \text{methyl, ethyl groups}\end{gathered} \quad (4b)$$

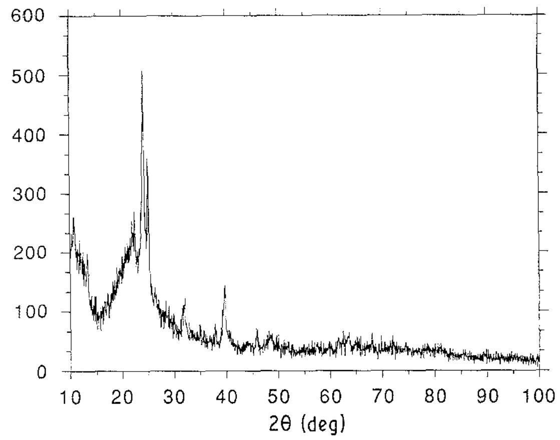

Figure 9 X-ray diffraction trace of borophosphosilicate gels heat treated at 650 °C for 12 h indicating the presence of crystalline BPO_4 and $Si_3(PO_4)_4$.

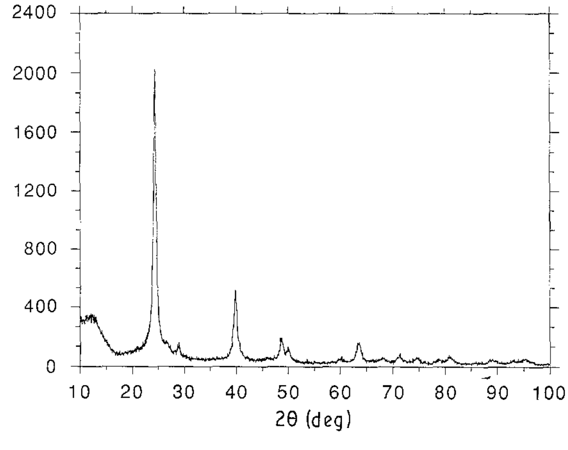

Figure 10 X-ray diffraction trace of borophosphate gels dried at 150 °C indicating the formation of crystalline BPO_4.

Trialkyl phosphate and trialkyl phosphite are both possible in the reaction of P_2O_5 with alcohol and in both cases the formation of the borophosphate linkage could be expected [42]. The formation of these linkages is more stable to attack by water and hence the formation of B_2O_3 seen in the case of borosilicate gels is not observed. We are currently in the process of investigating these reactions more rigorously and in this paper only preliminary results have been presented. Spectroscopic investigations are currently in process to understand the reaction and modification processes.

5. Conclusions

We have attempted to demonstrate the formation of borosilicate, borophosphosilicate and borophosphate gels using inexpensive methods without exercising any stringent control on atmospheric moisture. We have shown that the formation of borosilicate gels using boron oxide in alcohol is sensitive to the presence of atmospheric moisture; however, modification of the generated alkoxide using acacH results in the formation of homogeneous gels. In the case of borophosphosilicate gels, the loss in stoichiometry of the starting precursors results in the crystallization of two phases of BPO_4 and $3SiO_2 \cdot 2P_2O_5$. It is possible to stabilize the boron alkoxide by reacting with phosphorus alkoxide before hydrolysis to precipitate BPO_4 directly without forming crystalline B_2O_3. The conclusions reflect the effect of atmospheric moisture on the reactivity of boron alkoxide, the potential of acacH modification and the stabilization of boron alkoxide in the presence of phosphorus to form borophosphate.

Acknowledgements

Acknowledgement is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society (grant PRF 25507-G3) for support of this research. We thank Mr Paul McMichaels for his help in the sol–gel synthesis experiments and Mr B. Pingitore, Department of Metallurgical Engineering and Materials Science, CMU, for assistance in preparation of samples and collection of infrared spectra. Ms Purnima Apte and Dr P. P. Phule, Department of Materials Science and Engineering, University of Pittsburgh, are also thanked for their assistance in conducting the differential thermal analysis experiments on our samples.

References

1. R. R. TUMMALA and E. J. RYMASZEWSKI (eds), "Microelectronic Packaging Handbook" (Van Nostrand Reinhold, New York, 1989).
2. G.GEIGER, *Bull. Amer. Ceram. Soc.* **69** (1990) 1131.
3. E. M. RABINOVICH, *J. Electron. Packaging* **111** (1989) 183.
4. R. R. TUMMALA and R. B. SHAW, in "High Tech. Ceramics", edited by P. Vincenzini (Elsevier Science, Amsterdam, 1987) p. 75.
5. J. L. SPRAGUE, *IEEE Trans. Compon. Hybrids Manufact. Technol.* **13** (1990) 390.
6. K. R. KINSMAN, *J. Metals* **6** (1998) 7.
7. R. R. TUMMALA, *J. Amer. Ceram. Soc.* **74** (1991) 895.
8. A. J. BLODGETT Jr, *Sci. Amer.* **249** (1983) 2.
9. J. F. MacDOWELL and G. H. BEALL, in Materials Research Society Symposium Proceedings, Boston, "Advanced Electronic Packaging Materials", edited by A. T. Barfknecht, J. P. Partridge, C. J. Chen and Che-Yu Li, Vol. 167 (MRS, 1989).
10. *Idem*, in "Proceedings of the 1st International Science and Technology Conference, Materials and Processes for Microelectronic Systems", Ceramic Transactions, edited by K. M. Nair, R. Pohanka and R. C. Buchanan, Vol. 15 (American Ceramic Soc. 1989) p. 259.
11. R. JABRA, J. PHALIPPOU and J. ZARZYCKI, *J. Non-Cryst. Solids* **42** (1980) 489.
12. A. D. IRWIN, J. S. HOLMGREN, T. W. ZERDA and J. JONES, *ibid.* **89** (1987) 191.
13. I. MATSUYAMA, K. SUSA, S. SATOM and T. SUGANUMA, UK Pat. Appl. GB 2041 913 (1980).
14. B. E. YOLDAS, *J. Non-Cryst. Solids* **63** (1984) 145.
15. I. MATSUYAMA, K. SUSA, T. SUGANUMA, T. KATOUYAMA and H. OBAYASHI, UK Pat. Appl. GB 2075 003 (1981).
16. S. P. MUKHERJEE, *J. Non-Cryst. Solids* **42** (1980) 477.
17. T. WOIGNIER, J. PHALIPPOU and J. ZARZYCKI, *ibid.* **63** (1984) 117.
18. M. PRASSAS and L. HENCH, in "Ultrastructure Processing of Ceramics, Glasses and Composites", edited by. L. Hench and D. R. Ulrich (Noyes, New Jersey, 1984) p. 100.
19. M. A. VILLEGAS, F. CAPEL and, J. M. FERNANDEZ NAVARRO, *J. Mater. Sci. Lett.* **7** (1988) 791.
20. M. NOGAMI, *Commun. Amer. Ceram. Soc* **67** (1984) C-258.
21. K. KATA, Y. SHIMADA and H. TAKAMIZAWA, in "6th IEEE/CHMT, International Electronic Manufacturing Technology Symposium Proceedings" (1989) p. 24.
22. B. E. YOLDAS, *J. Mater. Sci.* **14** (1979) 1843.
23. K. NIWA, Y. IMANAKA, N. KAMEHARA and S. AOKI, in Advances in Ceramics, "Ceramic Substrates and Packages For Electronic Applications", edited by M. F. Yan, K. Niwa, H. M. O'Bryan Jr and W. S. Young (1989) p. 323.
24. N. KAMEHARA, S. AOKI, Y. IMANAKA and K. NIWA, in "Proceedings of the MRS International Meeting on Advanced Materials", edited by M. Doyama, S. Somiya and R. P. H. Chang, Vol. 10 (1989) p. 153.
25. K. S. CHOU, *J. Non-Cryst. Solids* **110** (1989) 122.
26. D.C. BRADLEY, R. C. MEHROTRA and D. P. GAUR, "Metal Alkoxides" (Academic Press, London, 1978).
27. R. H. EWELL and H. INSLEY, *J. Nat. Bur. Stand.* **15** (2) (1935) 173.
28. A. K. KIJOWSKI, S. KOMARNENI and R. ROY, *Mater. Res. Soc. Symp.* **121** (1988) 245.
29. R. ROY, *J. Amer. Ceram. Soc.* **52** (1969) 145.
30. V. G. HILL, R. ROY and E. F. OSBORN, *ibid.* **35** (1952) 135.
31. R. ROY, *ibid.* **39** (1956) 145.
32. P. F. JAMES, *J. Non-Cryst. Solids* **100** (1988) 93.
33. J. D. MACKENZIE, *ibid.* **100** (1988) 162.
34. D. R. ULRICH, *ibid.* **100** (1988) 174.
35. H. SCHMIDT, *ibid.* **100** (1988) 51.
36. C. SANCHEZ, J. LIVAGE, M. HENRY and F. BABONNEAU, *ibid.* **100** (1988) 65.
37. J. ZARZYCKI, *ibid.* **121** (1990) 110.
38. M. NABAVI, S. DOEUFF, C. SANCHEZ and J. LIVAGE, *ibid.* **121** (1990) 31.
39. H. SCHMIDT and H. WOLTER, *ibid.* **121** (1990) 428.
40. P. P. PHULE and F. KHAIRULA, in "Proceedings of the Third International Conference on Powder Processing Science", San Diego, CA 4–6 February 1990, Ceramic Transactions, Vol. 12 (American Ceramic Society 1990)
41. M. NABAVI, S. DOUEFF, C. SANCHEZ and J. LIVAGE, *J. Non-Cryst. Solids* **121** (1990) 31-34.
42. F. A. COTTON and G. WILKINSON, "Advanced Inorganic Chemistry", 5th Edn (Wiley, New York, 1988).
43. M. NOGAMI and Y. MORIYA, *J. Non-Cryst. Solids* **48** (1982) 359.
44. M. GUGLIELMI and G. CARTURAN, *ibid.* **100** (1988) 16.

Received 12 February
and accepted 6 July 1992