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Modified oxide sol–gel (MOSG) synthesis of borophosphosilicate glasses and glass-ceramics

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A modified oxide sol–gel (MOSG) process was used to synthesize borophosphosilicate glasses and glass-ceramics using boron oxide and phosphorous pentoxide as starting precursors. The oxide precursors were used to form alkoxides *in situ*, which were then hydrolysed and condensed to form borophosphosilicate gels. The dried gels were analysed for their thermal properties and were heat treated accordingly, at a temperature of 800 °C, to crystallize the boron phosphate phase. The resultant xerogels were then analysed for their microstructure. Both pressureless and hot-pressing techniques were used to sinter the calcined gels to form glass-ceramics. The sintered samples were characterized for their microstructure using electron microscopy and evaluated for their dielectric properties. Dielectric measurements indicate that the sintered glass-ceramics possess dielectric constants less than 5 and dissipation factors less than 0.001 at a frequency of 1 MHz. The results of these studies show the potential of the oxide sol–gel- derived borophosphosilicate glass–ceramics for use as substrate materials in microelectronic packaging.

1. Introduction

There has been an increasing interest in glasses and glass-ceramics in the field of microelectronic packaging for high-speed devices, because of their low dielectric constant (~ 5 at 1 MHz) and good thermal expansion match to silicon [1]. As a result, several glasses and glass-ceramic systems have been studied in the literature. Table I lists a few of these materials and also gives their thermal and electrical characteristics important for electronic packaging [2–6]. Recently, Macdowell and Beall [7] identified glass-ceramics in the borophosphosilicate system and synthesized these glasses using conventional glass-melting techniques. They measured the dielectric constants to be in the range 3.8–4.5 at 1 MHz and consequently highlighted these materials as potential candidate materials for electronic packaging [8].

Conventional glass-processing techniques, involving melting of individual elements or compounds, suffer from problems of volatilization and phase separation leading to the formation of inhomogeneous glasses. This problem is even more severe with systems involving the use of volatile oxides such as B_2O_3 and P_2O_5. With the advent of the sol–gel techniques these limitations have been eliminated to a large extent. The sol–gel reactions conducted in solution, allow for good molecular mixing which leads to the formation of stoichiometric crystalline ceramics and glasses uniform in composition. The flexibility afforded by the sol–gel route also allows for the generation of bulk monoliths, fine powders and even thin films by controlling the chemistry and kinetics of the reactions. In addition, the sol–gel reactions are conducted at room temperature and the rapid kinetics of nucleation with minimum growth lead to the formation of fine amorphous particles possessing high specific surface area. This causes the powders to be very reactive enabling subsequent reaction processes necessary to form the desired material to be conducted at much lower temperatures than those required for the materials synthesized using the conventional mix and fire approaches [9–16].

The traditional organic sol–gel approach typically consists in using metal alkoxides as precursors which undergo hydrolysis and condensation reactions in solution to form polymeric species. The species eventually condense to form the core oxide network structural units which, on heat treatment, result in the formation of an amorphous glass or the desired crystalline ceramic phase. The technique works very well for binary systems; however, there are problems when synthesizing materials containing several components. This is mainly due to the differences in the rates of hydrolysis exhibited by alkoxides of different metals. The problem becomes particularly noteworthy in the case of reactive metals with large affinity for oxygen such as those from the transition series, the group III elements (e.g. B, Al), and the rare-earths. Once in solution they tend to undergo preferential hydrolysis in the presence of relatively stable alkoxides such as

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TABLE I Properties of selected 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
$2MgO \cdot 2Al_2O_3 \cdot 5SiO_2 + (Al_2O_3)$*	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

* Crystalline ceramic phase.

those of silicon. As a result, molecular inhomogeneities arise which can lead to the formation of undesired phases. Subsequent prolonged heat treatments at high temperatures are therefore required to promote adequate diffusion of the components in the solid state to form the desired single-phase material. Despite these treatments, the presence of trace amounts of secondary phases can never be discounted, as we have seen in our current on-going work on sol–gel synthesis of cordierite [17].

One way of counteracting the problem is to complex the alkoxide and thus reduce the reactivity of the alkoxides. This control of reactivity is mainly brought about by the reduction in the partial positive charge on the metal species which makes it more stable towards hydrolysis. The most common complexing agent studied in the literature has been the use of chelating agents such as acetylacetonate (acacH) [18, 19]. An alternative approach would be to synthesize the alkoxide *in situ* using stable oxide precursors. In an earlier paper, we demonstrated the use of metal oxides as starting precursors to form metal alkoxides *in situ*. The approach clearly demonstrated a novel and economic methodology to form homogeneous gels in the case of reactive group III and V alkoxides. Specifically, the technique consisted of reacting oxides of boron and phosphorus with alcohol to form partially hydrolysed alkoxides, as shown by the well-understood reactions below [20]

$$B_2O_3 + 6ROH \rightleftharpoons 2B(OR)_3 + 3H_2O$$

$$B(OR)_3 + xH_2O \rightleftharpoons B(OR)_{3-x}(OH)_x + xROH \quad (1)$$

$$P_2O_5 + 6ROH \rightleftharpoons 2[OP(OR)_3] + 3H_2O$$

$$OP(OR)_3 + xH_2O \rightleftharpoons OP(OR)_{3-x}(OH)_x + xROH (2)$$

where $0 < x < 3$, and R = alkyl group.

The advantage of the process is the use of stable boron oxide and phosphorous pentoxide precursors which react with alcohol to form partially hydrolysed soluble species. It is, however, very difficult to ascertain the extent of the hydrolysis reaction owing to the very reactive nature of boron and phosphorus. Following the in-situ synthesis of the alkoxides, hydrolysis and condensation can be induced in the same way as in the traditional sol–gel process [21]. The process conveniently avoids the use of reactive and volatile boron and phosphorous alkoxides and hence, provides an economic route to form homogenous glasses and glass-ceramics. The glasses produced by the oxide sol–gel approach can then be heat treated and sintered to arrive at the desired glass-ceramic. An earlier publication marked the first phase in an ongoing research programme to synthesize composites of glass-ceramics in the borophosphosilicate system [22]. In this paper, results of further studies conducted in this system are presented. The oxide approach was used to synthesize borophosphosilicate glass. Following similar procedures, the gel powders have been characterized for surface area and microstructure, and subsequently densified to form glass-ceramics. Electrical characterization of these glass-ceramics have also been conducted to determine the dielectric constant and dissipation factor. Electron microscopy has also been performed to examine the microstructure.

2. Experimental procedure

2.1. Glass synthesis

Borophosphosilicate glasses were synthesized using commercially obtained oxides of boron and phosphorus while using TEOS for silicon following the procedure very similar to that published earlier [22]. Stoichiometric quantities of the oxides and TEOS were reacted in the ratio of $B_2O_3:P_2O_5:SiO_2 = 1:1:4$. The exact procedure consisted in mixing equimolar amounts of B_2O_3 and P_2O_5 in a Nalgene beaker. All the necessary materials were then placed in a glove bag filled with nitrogen in order to create an inert atmosphere. This was needed to prevent the volatilization of boron alkoxide and the subsequent formation of crystalline boron oxide as a discrete phase, as indicated by our earlier studies. The glove bag was sealed, and the rest of the experiment was performed inside the bag itself. The oxide powders (B_2O_3 and P_2O_5) were then dissolved in 100 ml alcohol. The beaker was covered with parafilm, and the

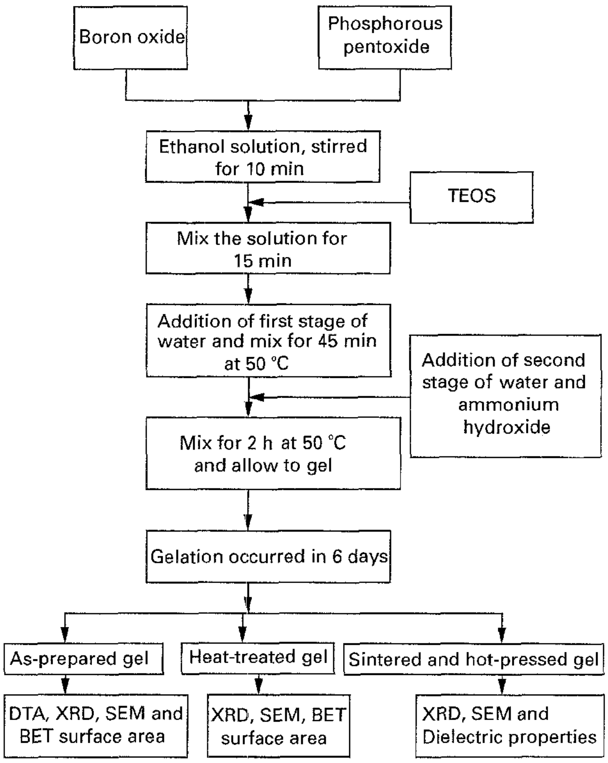

Figure 1 Flow sheet showing the procedure that was followed for synthesizing borophosphosilicate glasses and glass-ceramics.

contents stirred for 10 min until the powders dissolved. At this stage, ~ 22 ml TEOS was measured and added to the beaker containing B_2O_3 and P_2O_5, and the solution was mixed for 15 min. Water was then added to the resulting solution in two stages. The first stage consisted of adding 16 ml and stirring the solution for 45 min at 50 °C. The second stage consisted of adding a basic solution of water (16 ml) containing 10 drops of ammonium hydroxide. The entire solution was then mixed for 2 h at 50 °C. Gelation of the solution occurred in 6 days. A schematic diagram of the procedure used to synthesize borophosphosilicate glasses is shown in Fig. 1.

2.2. Heat treatment and thermal analysis

Differential thermal analysis (DTA) was performed using a Perkin–Elmer DTA. Approximately 70 mg dried gel was heated in air at a rate of 10 °C $\min^{-1}$ to 1000 °C. Heat treatment was performed based on the results of the DTA. The glass was crushed initially with a mortar and pestle and heat treated up to 800 °C for 36 h in a platinum crucible. The powder was then reground and heat treated at 800 °C for 24 h. Additional heat treatments at 800 °C for 24 h were also conducted after grinding the samples before finally heat treating the samples at 800 °C for 36 h. These heat treatments were essential to remove the carbon and to induce crystallization of the boron phosphate phase. The full heat-treatment profile is shown in Table II.

2.3. Sintering and hot pressing

The heat-treated powders were sintered with and without pressure. The heat-treated powders were cold isostatically pressed (sample 1) as well as cold-pressed into pellets (sample 2). Sample 1 was prepared by cold isostatically pressing the heat-treated powders using a pressure of 40 000 p.s.i. (10^3 p.s.i. = 6.89 N mm^{-2}) and then sintering initially at 1000 °C for 24 h followed by further sintering at 1100 °C for 72 h. Sample 2 was prepared by cold pressing the heat-treated powders using a pressure of 10 000 p.s.i. The cold-pressed pellets were then sintered at a temperature of 1100 °C for 144 h. Some of the heat-treated powder was also hot-pressed. The hot-press experiment was conducted using a 10 Ton Electrofuel (Toronto, Canada) hot-press at 1200 °C for 1 h employing a pressure of 4500 p.s.i. in an argon atmosphere.

TABLE II Heat-treatment schedule that was followed for the borophosphosilicate glass-ceramic

Temperature (°C)	Heating rate (°C per min)	Duration (h)
150	1	3
200	1	3
300	1	10
360	1	10
800	1	36
	Sample was reground	
800	5	24
	Sample was reground	
800	5	24
800	5	12

2.4. Characterization

X-ray diffraction (XRD) using a Rigaku θ/θ diffractometer and SEM analysis using a CamScan scanning electron microscope were performed on the as-prepared and heat-treated powders to identify the phases formed and observe the morphology of the gels. Hot-pressed and sintered gels were also examined for the evolution of crystalline phase and microstructure. Specific surface area of the as-prepared and heat-treated gels was determined using the Brunauer–Emmett–Teller (BET) technique. Dielectric measurements were conducted on the hot-pressed and sintered samples. Samples for dielectric measurements were prepared by grinding them into the approximate shape of a regular rectangular prism, and applying silver electrodes to the sample faces. The capacitance, C_m, and loss was measured using an HP 4275A multi-frequency LCR meter. The following formula was used to correct the capacitance for edge effect based on the earlier work reported by Field [23] and later modified by Subramanian *et al.* [24].

$$C_e = [0.019 \ln(P/t) - 0.043]P \qquad (3)$$

where P is the sample perimeter, and t the sample thickness. The capacitance for the sample, C, was then determined by subtracting C_e from C_m. Dielectric constants were then calculated using the corrected

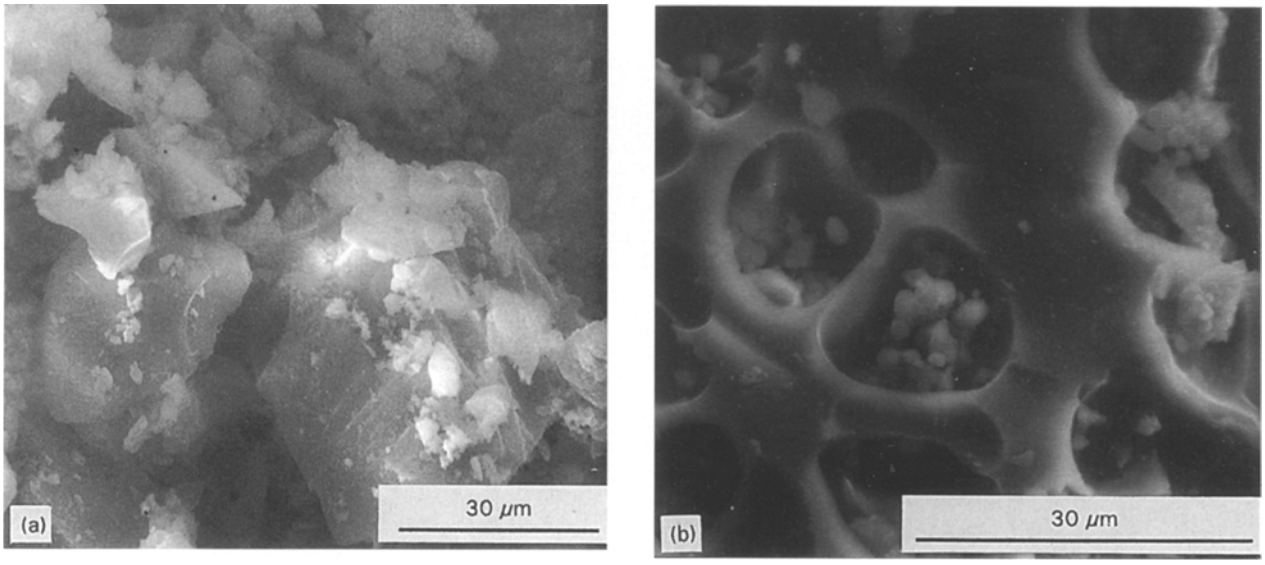

Figure 2 Scanning electron micrographs showing the morphology of the (a) as-prepared and (b) heat-treated (at 800 °C for 96 h) borophosphosilicate glass and glass-ceramic. Note the porous microstructure of the heat-treated gels due to the simultaneous processes of loss of carbon and softening of the glass. See text for more details.

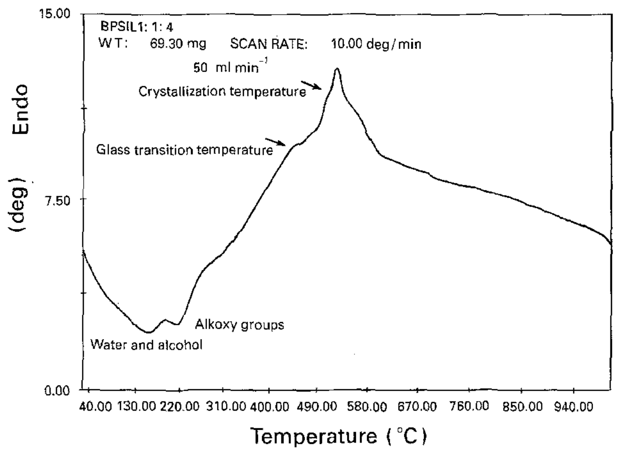

Figure 3 Differential thermal analysis plot obtained on the borophosphosilicate glasses heated in air at 10 °C min^{-1}. The endotherms correspond to loss of water, alcohol and the residual alkoxy groups, while the exotherm corresponds to the crystallization of the boron phosphate (BPO_4) phase.

capacitance with the following relationships

$$C = (A/t)\,E' \tag{4a}$$

$$K = E'/E_0 \tag{4b}$$

where K is the dielectric constant, E' the permittivity of the solid, and E_0 the permittivity of a vacuum.

3. Results and discussion

The gels prepared using the above procedure were dried in air and then characterized for their morphology using scanning electron microscopy. Fig. 2a shows a scanning electron micrograph of the as-prepared gel showing clusters of fine particles $\approx 30\ \mu m$ in size. Specific surface area analysis was also conducted on the as-prepared gels using the BET technique. The surface area values obtained were consistent with the SEM analysis. The results of the analysis indicate a high specific surface area of 94.67 $m^2\,g^{-1}$, which is typical of alkoxide-derived xerogels. The gels were then characterized for their thermal stability using differential thermal analysis. Fig. 3 shows a DTA profile obtained by heating the as-prepared gel in air using a ramp rate of 10 °C min^{-1}. The profile shows the possible occurrences of the following physical processes. The endotherm which initiates at approximately 70 °C could be attributed to the gradual loss of alcohol as a result of the condensation reaction in the gel [25]. Another endotherm at approximately 180 °C can be related to the loss of water from the condensation reactions and the residual alkoxy groups from the sample. As the sample is heated, the occurrence of the glass transition temperature is seen by the endotherm around 430 °C followed by crystallization at 490 °C.

XRD was, therefore, performed on the gels to characterize the thermal changes shown in the DTA. Fig. 4a shows an XRD profile obtained on the as-prepared gels indicating the amorphous nature. Following heat treatment at 800 °C for 96 h, XRD was also conducted on the heat-treated gel, the pattern for which is also shown in Fig. 4b. The formation of BPO_4 upon crystallization of the gel is clearly seen from the diffraction trace. Thus, the XRD analysis conducted on the as-prepared and heat-treated samples supports the thermal analysis results.

Once the samples were crystallized, their morphology was again analysed using SEM. Fig. 2b shows the porous nature of the heat-treated gels. This could be expected, because the glass transition temperature for the composition and the crystallization of the BPO_4 phase occur at very close temperature intervals. Moreover, both of these processes overlap with the temperature range (400–700 °C) most favoured for carbon removal. One can therefore envisage the formation of porosity due to the loss of carbon from the softened gels. Specific surface area measurements conducted on the heat-treated sample revealed a significant decrease in surface area to 0.1224 $m^2\,g^{-1}$ corresponding to the

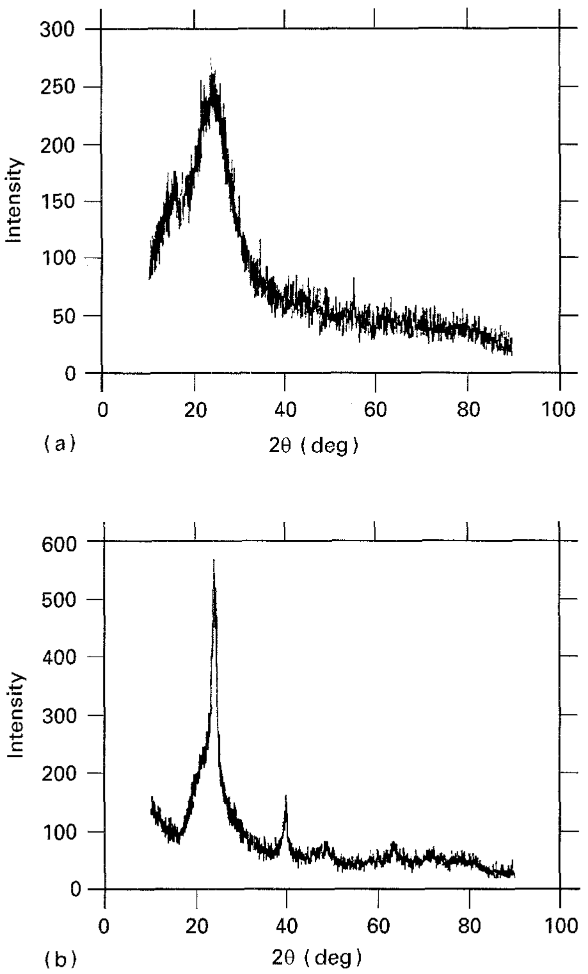

Figure 4 X-ray diffraction traces obtained on (a) the as-prepared gels showing the amorphous nature and (b) the heat-treated gels 96 h (at 800 °C) for showing the presence of the crystalline boron phosphate (BPO_4) phase.

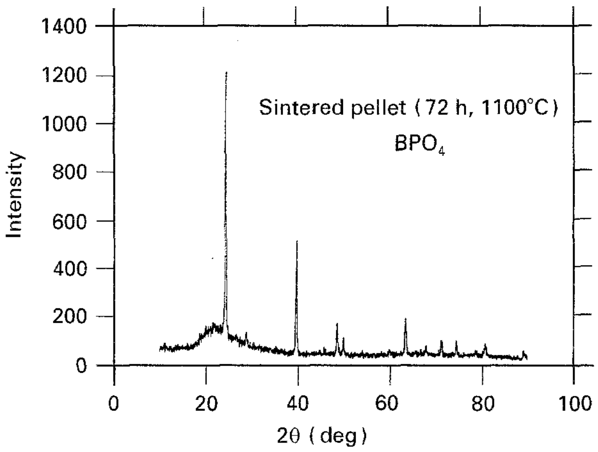

Figure 5 X-ray diffraction profile obtained on the sintered borophosphosilicate glass-ceramic showing intense peaks for BPO_4 phase indicating the growth of the boron phosphate crystallites.

crystallization and growth of boron phosphate. The sample was initially sintered at 1000 °C for 24 h and then sintered at 1100 °C for an additional 72 h. The XRD profile obtained on the sintered sample, shown in Fig. 5, reveals even sharper peaks corresponding to the growth of boron phosphate crystallites.

The sintered samples showed a fair amount of visible porosity mainly due to the entrapment of air and the formation of CO and CO_2 as the carbon in the gels reacts with oxygen. The loss of these gases becomes increasingly difficult due to the viscous nature of the glass and hence, they remain trapped in the softened gels. Prolonged homogenization treatments are therefore necessary to eliminate the bubbles. However, even after considerable heat treatments, complete removal of the trapped bubbles is extremely difficult. The presence of porosity, although conducive to obtaining low dielectric constants, is deleterious to achieving good strength and mechanical integrity. Therefore, hot-pressing experiments were conducted by pressing samples using a pressure of 4500 p.s.i. at 1200 °C for 1 h in argon. The hot-pressed glass-ceramic was examined for its microstructure using SEM after the sample surface was etched with 1 M HF acid. The analysis revealed an overetched specimen surface exhibiting small particles of crystallized boron phosphate in a dense glass matrix as shown in Fig. 6. The micrographs also reveal a noticeable decrease in porosity for the hot-pressed sample, which will provide for improved structural and mechanical properties.

Dielectric studies were then conducted on all the sintered and hot-pressed samples. The results of dielectric measurements conducted for pressurelessly sintered and hot-pressed samples are shown in Table III. As can be seen, the samples exhibit dielectric values in the range 3.94–4.36 and dissipation factors of 0.0007–0.0010 at a frequency of 1 MHz. Sample 2, in fact, showed a much lower dielectric constant (3.94) as opposed to sample 1 even though it was sintered for a considerably longer time. This could be due to the fact that sample 2 had been prepared by sintering the cold-pressed dried gel powders, while sample 1 had been prepared by sintering the cold isostatically pressed powders. The presence of a large amount of initial porosity in sample 2, coupled with the viscous nature of the glass, makes it extremely difficult to eliminate the pores completely despite long sintering times. Thus, although both samples had a fair amount of porosity, it can be expected that sample 2 had a larger amount of porosity in comparison with sample 1, which is reflected in this lower dielectric constant. Future work is being directed towards systematically monitoring the porosity and studying its effect on the dielectric constant. On the other hand, measurements on the hot-pressed sample indicate dielectric values of 4.25 at 1 MHz with a dissipation factor of 0.0018. There seems to be no significant deviation in the dielectric constant values due to hot-pressing, although there is a significant reduction in porosity (see Fig. 6). Nevertheless, the dielectric constant of the densest sample obtained by hot pressing is less than 4.5, suggesting the potential of these materials as substrates in microelectronic packaging.

4. Conclusion

A novel modified oxide sol–gel (MOSG) approach was used to synthesize homogeneous borophosphosilicate glasses and glass-ceramics using boron oxide and phosphorous pentoxide as precursors. In

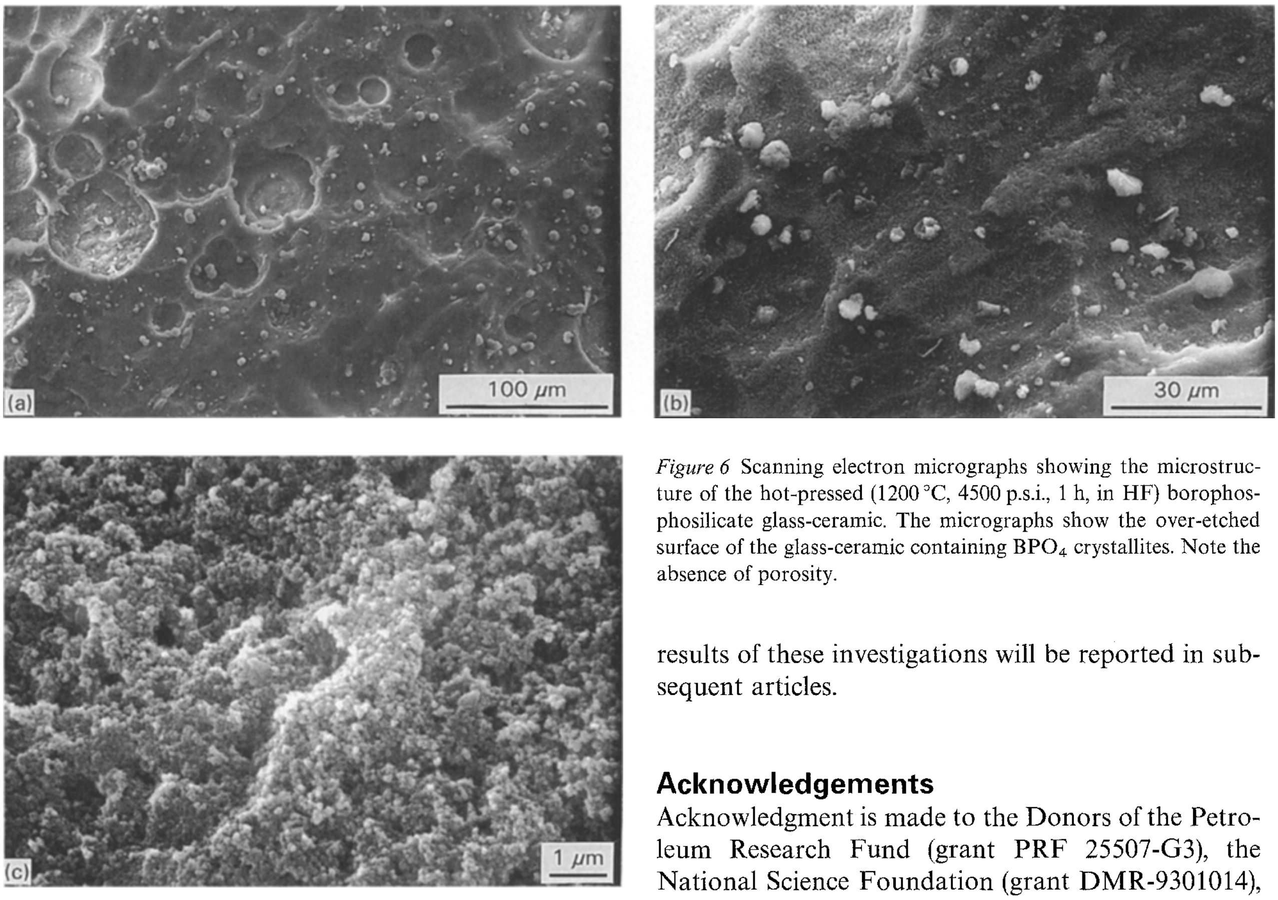

Figure 6 Scanning electron micrographs showing the microstructure of the hot-pressed (1200 °C, 4500 p.s.i., 1 h, in HF) borophosphosilicate glass-ceramic. The micrographs show the over-etched surface of the glass-ceramic containing BPO_4 crystallites. Note the absence of porosity.

accordance with DTA results, the gels were heat treated to 800 °C to crystallize boron phosphate. The crystallized gels were then sintered (1100 °C, 72 and 144 h) and hot-pressed (1200 °C, 1 h) to obtain borophosphosilicate glass-ceramics. Samples sintered after cold pressing showed a significantly larger amount of porosity and a much lower dielectric constant (3.94) than the cold isostatically pressed and sintered (4.36) samples. Hot pressing of the dried gels resulted in reduced porosity and a dielectric constant of 4.25. These dielectric values of less than 4.5 suggest the potential of these materials as substrates for electronic packaging. We are currently in the process of investigating other compositions in the system and studying their microstructure and dielectric properties. The results of these investigations will be reported in subsequent articles.

Acknowledgements

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TABLE III Dielectric constant and dielectric loss measured for the pressurelessly sintered and hot-pressed glass-ceramic samples

Sample	Sintering conditions	Measured at 100 kHz		Measured at 1 MHz	
		Dielectric constant	Dissipation factor	Dielectric constant	Dissipation factor
1	Cold isostatic press, 40 000 p.s.i. Sinter in air 1000 °C, 24 h 1100 °C, 72 h	4.37	0.0015	4.36	0.0007
2	Cold pressed 10 000 p.s.i. Sinter in air 1100 °C, 144 h	3.94	0.0019	3.94	0.0010
3	Hot-pressed argon 1450 °C 4500 p.s.i.	–	–	4.25	0.0018

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