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Modified Oxide Sol-Precipitation (MOSP) Approach for Synthesizing Borophosphosilicate Glasses and Glass−Ceramics

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A modified oxide sol-precipitation process (MOSP) was used to synthesize borophosphosilicate glasses and glass−ceramics utilizing boron oxide and phosphorous pentoxide precursors. The oxide precursors were used to form alkoxides in situ, which were then partially hydrolyzed. Excess ammonium hydroxide was added to initiate a precipitation reaction. The resultant precipitate was centrifuged and separated from the supernatant liquid. The thermal properties of the dried precipitates were analyzed and the precipitates were accordingly heat treated to 800 °C, in order to crystallize the boron phosphate phase. Pressureless sintering was used to sinter the powders and form glass−ceramics. Microstructures of the sintered samples were then characterized using electron microscopy, and the dielectric properties were measured. Dielectric measurements indicate that the sintered glass−ceramics possess dielectric constants less than 4.0 and dissipation factors less than 0.001 at a frequency of 1 MHz. Results of these studies show that the modified oxide sol-precipitation is a viable approach for synthesizing borophosphosilicate glass−ceramics for use as substrate materials in microelectronic packaging.

Introduction

Glasses and glass−ceramics are known to possess low dielectric constants (∼5 at 1 MHz).[1] They have been investigated as candidate substrate materials for electronic packaging of high speed devices. In particular, glasses and glass−ceramics have been extensively studied for their application as substrates in the Flip-Chip technology developed by IBM.[1,4] Table 1 lists a few of these materials that have been widely studied and also outlines their thermal and electrical characteristics important for electronic packaging.[2−6] Macdowell and Beall[7] recently identified glass−ceramics in the borophosphosilicate system. They synthesized these glasses using conventional glass-melting techniques and determined their dielectric constants to be in the range 3.8−4.5 at 1 MHz. Consequently, they highlighted these glass−ceramics to be potential candidate materials for electronic packaging of high-speed devices.[8]

Table 1. Properties of Selected Glasses, Glass + Ceramics, and Glass−Ceramics

materials	dielectric constant	coeff of thermal expansion (10^{-7}/°C)
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
$MgO + SiO_2 + B_2O_3 + Al_2O_3 + (Al_2O_3)$	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

While conventional melting techniques generally provide an economical method for processing large batches of glasses, there are problems associated with this method, particularly in relation to certain systems. One of the problems encountered is phase separation leading to the formation of inhomogeneous glasses. Another problem is volatilization of reactants, which is intensified with compositions involving the use of

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volatile oxides such as B_2O_3 and P_2O_5. Many of the problems associated with the conventional glass and glass–ceramic processing methods can be circumvented by using low-temperature chemical processing techniques. Several low-temperature chemical routes have been studied in recent years. Among these routes, the precipitation reaction is perhaps the most common. The precipitation reactions are conducted in solution, which allows for good mixing at the molecular level. As a result, stoichiometric crystalline ceramics and glasses uniform in composition can be synthesized. In addition, the reactions occur at room temperature, and by using the appropriate catalysts the kinetics of the reaction can also be controlled to synthesize fine amorphous particles possessing high specific surface area. Thus, the powders are very reactive and can subsequently be processed to generate the desired material at much lower temperatures than those required using conventional "mix and fire" approaches.[9–16]

The aqueous precipitation route is very common and has been known for several years. However, the application of nonaqueous precipitation approaches for synthesizing ceramics have emerged with the advent of the sol–gel process. Traditional sol–gel process involves the formation of a sol which is slowly transformed to a gel via several intermediate reactions. However, these reactions can be accelerated to result in a precipitate through a process aptly called sol-precipitation. The sol-precipitation process, similar to the sol–gel method, is an equally powerful technique for synthesizing fine powders.

Typically, the sol–gel process consists of using metal alkoxides precursors in alcohol solutions which undergo hydrolysis and condensation reactions to form polymeric species. The species eventually condense to form the core oxide network structural units which on heat treatment lead to 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 variation in the rates of hydrolysis exhibited by different metal alkoxides. The problem becomes particularly severe in the case of reactive metals with a large affinity for oxygen such as those from the transition series, the group III elements, and the rare earths. Once in solution they tend to undergo preferential hydrolysis in the presence of relatively stable alkoxides such as those of silicon. As a result, molecular inhomogeneities arise which lead to 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 was demonstrated in our earlier published work on the sol–gel synthesis of cordierite.[17]

One way of counteracting this problem is to complex the alkoxide and thus reduce its reactivity. 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 toward hydrolysis. The most common complexing agent studied in the literature has been acetylacetonate (acacH).[18,19] However, an alternative approach would be to synthesize the alkoxide in situ using stable oxide precursors. In an earlier paper we had demonstrated the use of metal oxides as starting precursors to form metal alkoxides in situ. The approach, known as the modified oxide sol–gel (MOSG) process, clearly demonstrated a novel and economical route in comparison to the conventional metal alkoxide based sol–gel approach to form homogeneous gels in the case of reactive group III and group V metal alkoxides. Specifically, the technique consisted of reacting oxides of boron and phosphorous with alcohol to form partially hydrolyzed alkoxides. These reactions are well understood and are indicated below:[20]

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

$$B(OR)_3 + H_2O \Leftrightarrow B(OR)_{3-x}(OH)_x + xROH$$

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

$$[OP(OR)_3] + H_2O \Leftrightarrow OP(OR)_{3-x}(OH)_x + xROH$$

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

The advantage of this process is the use of stable boron oxide and phosphorous pentoxide precursors, which react with alcohol to form partially hydrolyzed species. However, due to the release of water as a reaction byproduct, it is very difficult to ascertain the extent of the hydrolysis reaction. Nevertheless, the partially hydrolyzed species can undergo complete hydrolysis and condensation similar to the traditional sol–gel process.[21] In addition, the kinetics of the reaction can be accelerated by the use of a base to initiate the sol-precipitation reaction and precipitate the condensed product. It is essential that initial condensation of the partially hydrolyzed alkoxides of different species be initiated prior to addition of the base to prevent preferential precipitation of the different alkoxide units. Such a prehydrolysis and condensation step would facilitate the homogeneity of the resultant gels. An added advantage of the sol-precipitation reaction is the large reduction in residual alkoxy groups retained in the sample. Due to the rapid condensation reaction, most of the organics remain dissolved in the solvent, which can be separated by filtration. Thus, the precipitated oxide product will contain reduced amounts of carbon.

The sol-precipitation approach also conveniently avoids the use of highly reactive, expensive, and volatile boron

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and phosphorous alkoxides and hence provides an economical route to form homogeneous glasses and glass–ceramics. The glasses produced by the sol-precipitation approach can then be heat treated and sintered to arrive at the desired glass–ceramic. Earlier publications marked the first phase in an ongoing research program to synthesize composites of glass–ceramics in the borophosphosilicate system.[22,23] In this paper, results of further studies conducted in this system utilizing a modified oxide sol-precipitation (MOSP) process are presented. The precipitation reaction was used to synthesize borophosphosilicate gel powders, and the powders were subsequently densified to form glass–ceramics. The dielectric constant and dissipation factors of the glass–ceramics were measured, and the microstructure of the sintered glass–ceramics was examined using scanning electron microscopy.

Experimental Procedure

Glass Synthesis. Borophosphosilicate glasses were synthesized using commercially available oxides (Johnson Matthey) of boron and phosphorous and TEOS (Aldrich) as the source of silicon. The procedure followed was similar to that outlined in our previous work.[22,23] The gels were prepared from stoichiometric quantities of the oxides and TEOS in the molar ratio of B_2O_3:P_2O_5:SiO_2 = 1:1:4 and 1:1:6. Equimolar amounts of B_2O_3 and P_2O_5 were mixed in a glass beaker, and the oxide powders (B_2O_3 and P_2O_5) were then dissolved in 100 cm^3 of ethanol. The beaker was covered with parafilm, and the contents stirred for 10 min until the powders dissolved. At this stage, $\sim$22 cm^3 of TEOS was added to the beaker containing B_2O_3 and P_2O_5, and the solution was mixed for 15 min. Water was then introduced to the resulting solution in two stages. The first stage consisted of adding 16 cm^3 and stirring the solution for 45 min at 65 °C to induce the formation of metal oxide linkages. The second stage consisted of adding a basic solution of water (16 cm^3) containing 25 cm^3 solution (14.8 N) of ammonium hydroxide, which induced a precipitation reaction. The solution was centrifuged to collect the precipitate which was then dried at 150 °C for 2 h. Figure 1 shows a schematic of the steps followed to synthesize the borophosphosilicate glasses.

Heat Treatment and Sintering. The precipitates were heat-treated to temperatures determined from previous DTA results that have been published elsewhere.[23] Accordingly, the precipitates were crushed with a mortar and pestle and heat-treated up to 800 °C for 24 h on a platinum foil. These heat treatments were essential to induce crystallization of the tetragonal boron phosphate phase and to eliminate any traces of residual carbon. The complete heat-treatment profile is shown in Figure 2.

The heat-treated powders corresponding to the two compositions, 1:1:4 and 1:1:6, were cold-pressed into pellets using a pressure of approximately 10 000 psi. The cold-pressed pellets were then sintered in air at a temperature of 1000 °C for 72 h.

Materials Characterization. X-ray diffraction (Rigaku θ/θ diffractometer) analysis was performed on the as-prepared and heat-treated gels to identify the presence of any crystalline phases. Specific surface area of the as-prepared and heat-treated gels was determined using the Brunauer–Emmett–Teller (BET) technique. Scanning electron microscopy (SEM) analysis was performed on the sintered samples to observe the microstructure using a CamScan scanning electron microscope. Dielectric measurements were also conducted on the 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 were measured using an HP 4275A multifrequency LCR meter. The following formula was used to correct the capacitance for edge effects based on the earlier work reported by Field[24] and later modified by Subramanian et al.:[25]

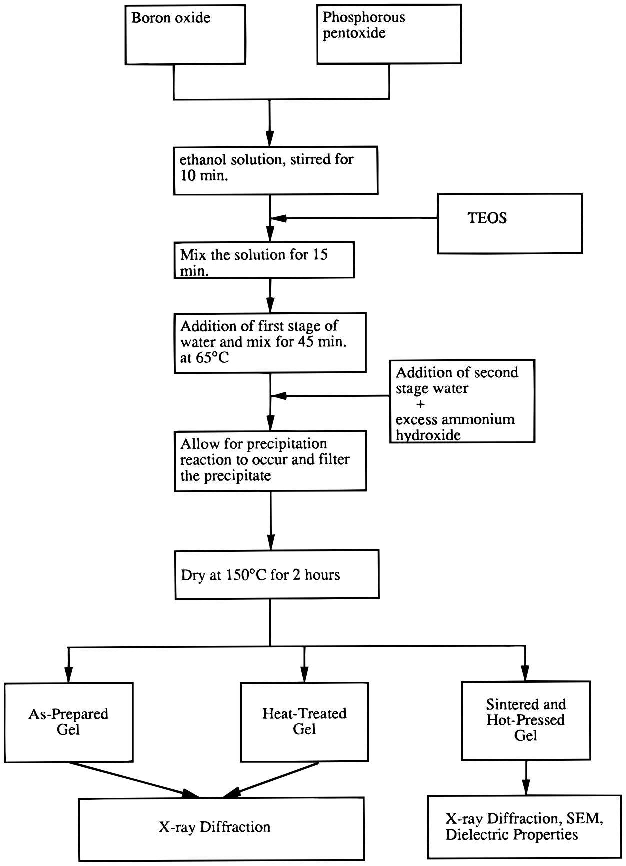

Figure 1. Flow sheet showing the procedure used for synthesizing borophosphosilicate gel powders.

Temperature (°C)	Heating Rate (°C/min)	Duration (hrs.)
150	1	5
200	1	5
300	1	10
400	1	24
800	1	24

Figure 2. Heat treatment profile followed to crystallize the borophosphosilicate gels.

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

where P = sample perimeter and t = sample thickness.

The capacitance of the sample, C, was then determined by subtracting C_e from C_m. Dielectric constants were calculated from the corrected capacitance using the following relationships:

$$C = (A/t)E' \qquad K = E'/E_0$$

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

Results and Discussion

Two glass compositions corresponding to B_2O_3:P_2O_5:SiO_2 = 1:1:4 and B_2O_3:P_2O_5:SiO_2 = 1:1:6 were studied

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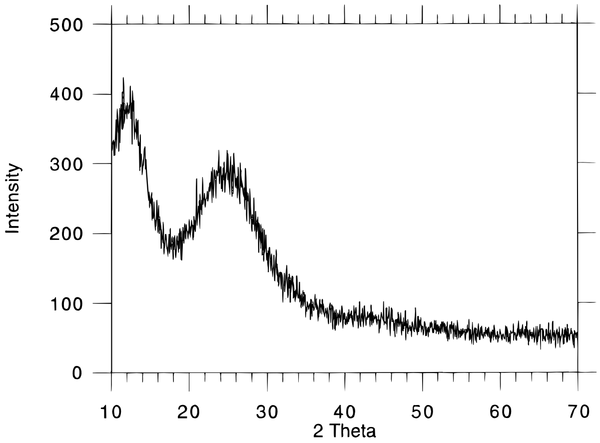

Figure 3. X-ray diffraction trace of 1:1:4 composition as-prepared gel.

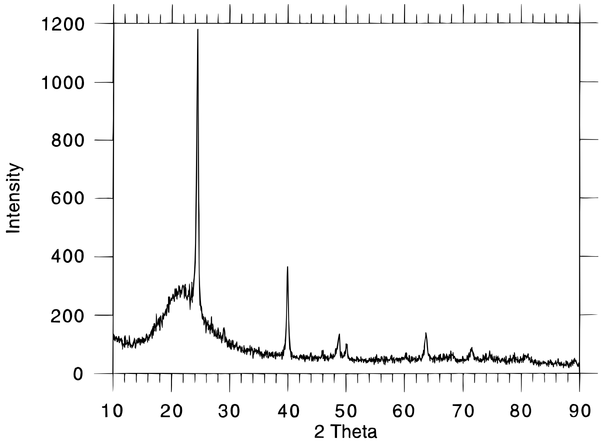

Figure 4. X-ray diffraction trace of 1:1:4 composition heat treated gel.

in the present work. The latter composition containing larger amounts of silica was selected to see its effect on the crystallization of the boron phosphate (BPO_4) phase. The results of characterization of these two glass compositions are discussed below.

Synthesis and Characterization of B_2O_3:P_2O_5:SiO_2; 1:1:4 Composition. The glasses were heat-treated to temperatures that were determined from previous results of differential thermal analysis (DTA) conducted on corresponding gels prepared using the modified oxide sol–gel process (MOSG). These results have already been published elsewhere.[23]

The powders were analyzed by XRD at each stage of heat treatment. Figure 3 shows the XRD trace obtained on the 1:1:4 as-prepared powders indicating their amorphous nature. The amorphous state of the as-prepared powders reflects the rapid condensation of the partially hydrolyzed alkoxy groups with minimum growth of the condensed oxide units at room temperature. The amorphous powders were heat-treated up to 800 °C for 24 h according to the profile shown in Figure 2. The heat-treated powders were then examined using X-ray diffraction analysis, the pattern for which is shown in Figure 4. In accordance with our previous studies conducted on gels with identical composition, BPO_4 is seen to crystallize from the amorphous gels.[23] Although the heat-treatment temperature was above the softening point of the calcined gel powders, it should be noted that due to the removal of significant amounts of residual organic groups during filtration, the calcined powders lose the remaining residual carbon very easily. This was clearly visible by the snow white color of the powders observed after calcination. On the other hand, gels of the same composition produced with the MOSG process required prolonged heat treatment at the same temperatures to eliminate the residual organics. Even after these long heat treatments, the MOSG powders still appear pale white, suggesting the retention of some carbon. In this regard, MOSP is an effective synthesis technique and results in powders containing much lower carbon content. The calcined heat-treated powders were then sintered at 1000 °C for 72 h in air and also analyzed for the presence of the crystalline BPO_4 phase using X-ray diffraction. Figure 5 shows an x-ray diffraction trace obtained on the sintered samples. As can be seen, the sintered sample shows a strong continuing presence of the crystalline BPO_4 phase.

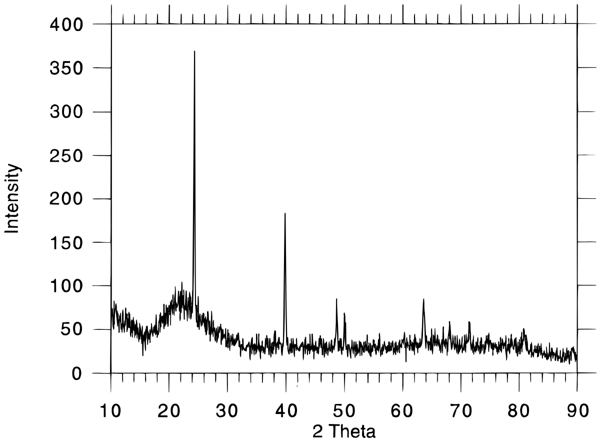

Figure 5. X-ray diffraction trace of 1:1:4 composition sintered glass–ceramic.

The cross section of a sintered 1:1:4 sample was then examined to observe the crystalline microstructure using SEM. The sample surface was over-etched with 1 M HF acid in order to better observe the BPO_4 crystallites. Figure 6 shows the micrographs obtained on the 1:1:4 sample. The micrographs show the presence of small submicron sized (<0.5 μm) crystallites in a glass matrix. Energy-dispersive X-ray analysis (EDAX) was also performed on the 1:1:4 sample and the X-ray traces collected are shown in Figures 7 and 8. The traces clearly show the presence of a large amount of silicon in the matrix and significant concentrations of phosphorous in the particles. These results suggest that the matrix phase is essentially a borophosphosilicate glass with high silicon content, while the particles correspond to crystallized boron phosphate. EDAX analysis is, therefore, consistent with the X-ray diffraction results obtained on the sintered 1:1:4 sample. The sintered sample also showed a small amount of visible porosity. The presence of porosity is known to be conducive for obtaining low dielectric constants as shown in our earlier work,[23] but can be deleterious for achieving good strength and mechanical integrity in the ceramic. However, the sintered glass–ceramic obtained using the MOSP process showed a significant reduction in porosity compared to the glass–ceramics produced through the MOSG process. This improvement is probably linked to the fact that many of the problems associated with the removal of carbon encountered in earlier MOSG experiments are avoided in the MOSP

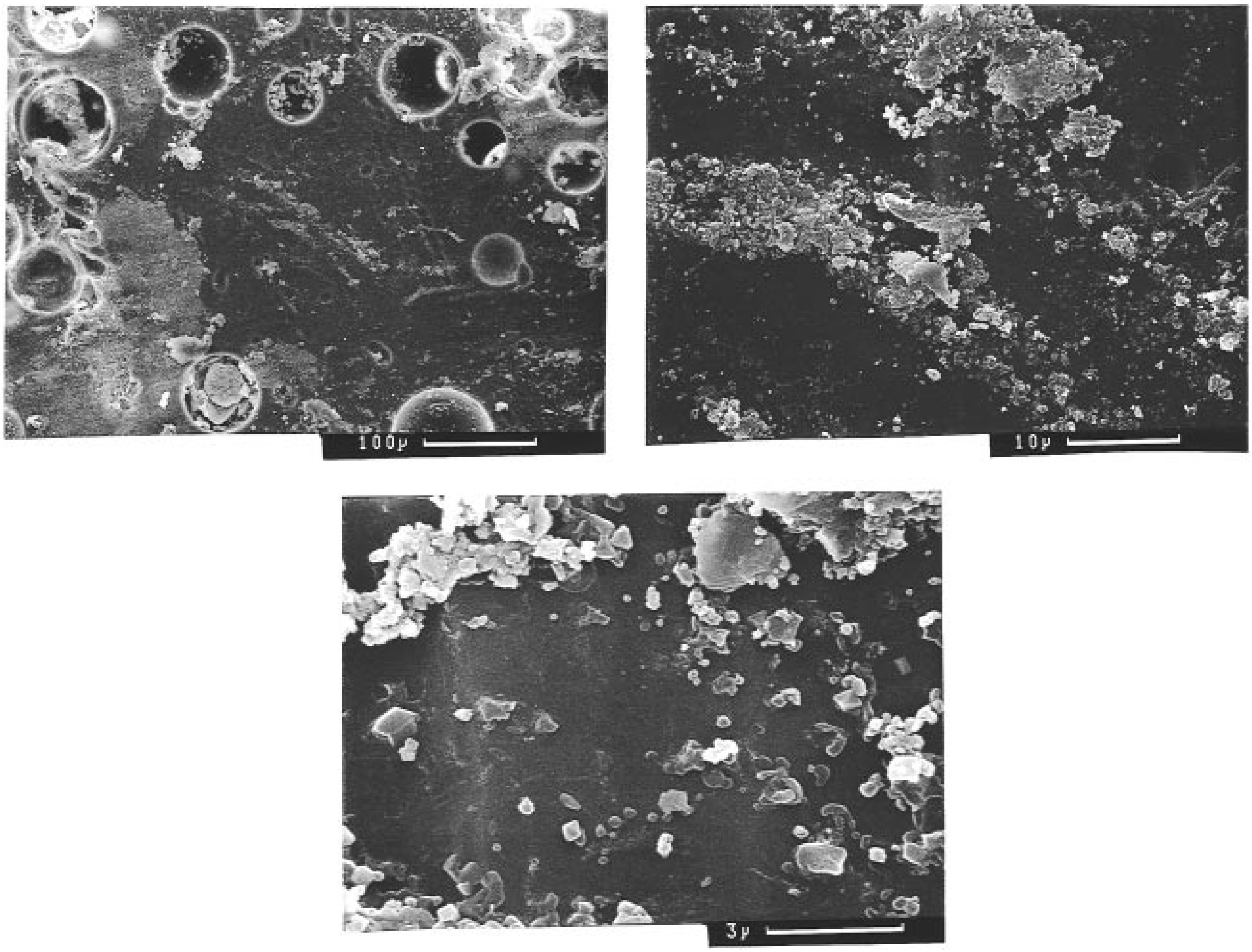

Figure 6. Micrographs showing the microstructure of a sintered sample of 1:1:4 composition at different magnifications.

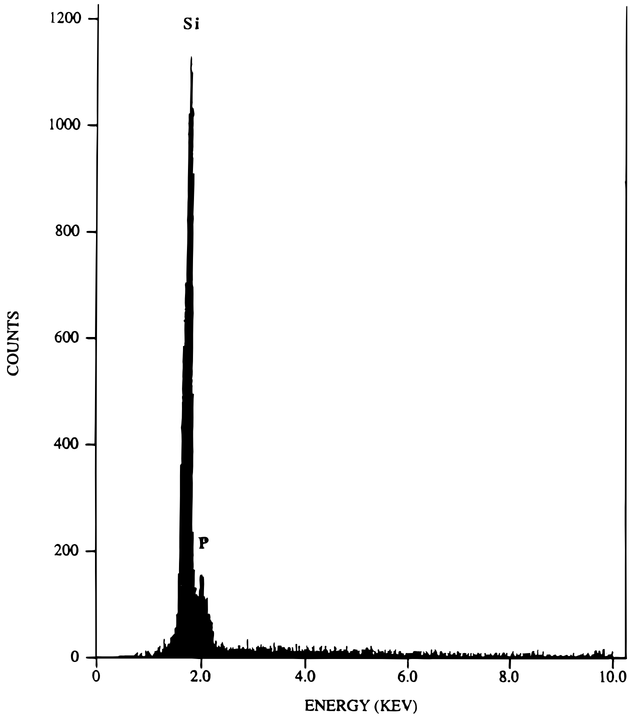

Figure 7. Results of energy-dispersive X-ray spectroscopy performed on the matrix of a sintered glass–ceramic of 1:1:4 composition.

approach. The precipitation reaction forces the separation of the condensed alkoxide units from alcohol and water. As a result, the powders have a reduced amount

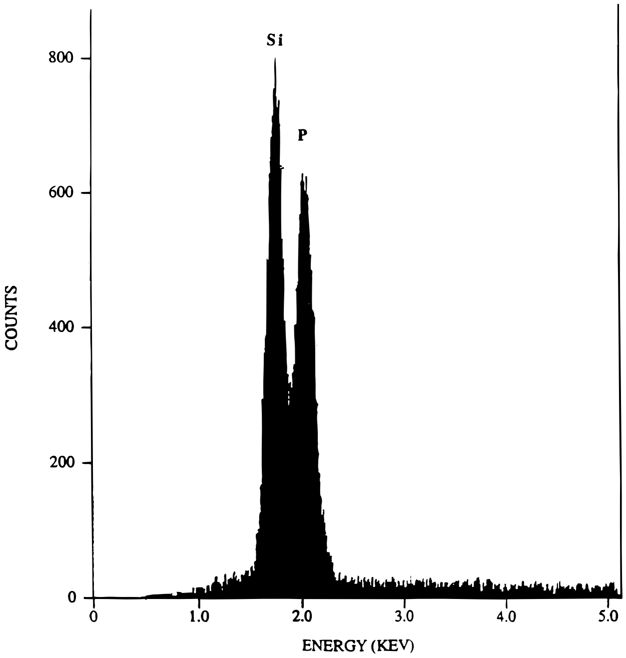

Figure 8. Results of energy-dispersive X-ray spectroscopy performed on the particles in a sintered glass–ceramic of 1:1:4 composition.

of residual carbon, which results in a much smaller volume fraction of bubbles caused by the formation and escape of carbon dioxide.

To better understand the electrical properties of the 1:1:4 composition samples, dielectric measurements

Table 2. Dielectric Constant and Dielectric Loss of Pressurelessly Sintered Borophosphosilicate Glass−Ceramics

	dielectric constant-edge corrected[a]		loss tangent	
composition	at 100 kHz	1 MHz	at 100 kHz	at 1 MHz
1:1:4	3.86	3.86	0.0006	0.0007
1:1:6	3.77	3.78	0.0010	0.0008

[a] The above dielectric values represent an average value taken of three samples for each composition. The dielectric value of each sample was measured three times for consistency.

were conducted on several pressurelessly sintered samples. The results of these dielectric measurements are shown in Table 2. As can be seen, the samples corresponding to the 1:1:4 composition exhibit an average dielectric value of 3.86 and an average dissipation factor of 0.0007 both taken at a frequency of 1 MHz. Despite the reduced porosity in the samples, these values are lower than those obtained on the gels of corresponding composition prepared using the MOSG process (3.94−4.36 and dissipation factors of 0.0007−0.0010 at a frequency of 1 MHz). This reduction of dielectric constant values is a reflection of the difference in the volume fraction of the crystallized BPO_4 phase, and the corresponding larger volume fraction of the glassy phase in the MOSP-derived powders. The reduction in the volume fraction of crystallized BPO_4 could occur due to either differences between the gel structures of MOSP and MOSG powders or the loss of boron and phosphorous as soluble hydrolyzed species in the filtrate. Detailed chemical and structural analysis would have to be conducted on the gels to identify the exact cause of this anomalous behavior.

Synthesis and Characterization of B_2O_3:P_2O_5:SiO_2; 1:1:6 Composition. As was the case with the 1:1:4 composition, X-ray diffraction was also used to examine the 1:1:6 composition powders. Similar to the 1:1:4 case discussed above, the results of the X-ray analysis indicate the as-prepared precipitate of the 1:1:6 composition to be amorphous. Accordingly, the gel powders were heat-treated following the heat-treatment profile shown in Figure 2. Heat treatment of the 1:1:6 composition gel powders similar to the 1:1:4 composition powders also leads to the crystallization of BPO_4, as indicated by the X-ray results. The heat-treated powders were then sintered at 1000 °C for 72 h in air. The sintered sample was also examined by X-ray diffraction, and as expected, the results indicate the presence of BPO_4; however, the intensity of the peaks corresponding to BPO_4 were much lower in comparison to the sintered samples of the 1:1:4 composition (Figure 5). This decrease in intensities can be attributed to a smaller volume fraction of BPO_4 crystallizing from the glass matrix. This can be expected since the driving force for crystallization of BPO_4 in the presence of relatively large amounts of a good glass former such as silica is rather poor. As a result, a large fraction of the boron and phosphorous remain associated with silicon in the amorphous state. The results of the SEM analysis also support this conclusion. The cross-sectional micrographs of the overetched 1:1:6 sample, shown in Figure 9, reveal only a small amount of crystalline BPO_4 in the

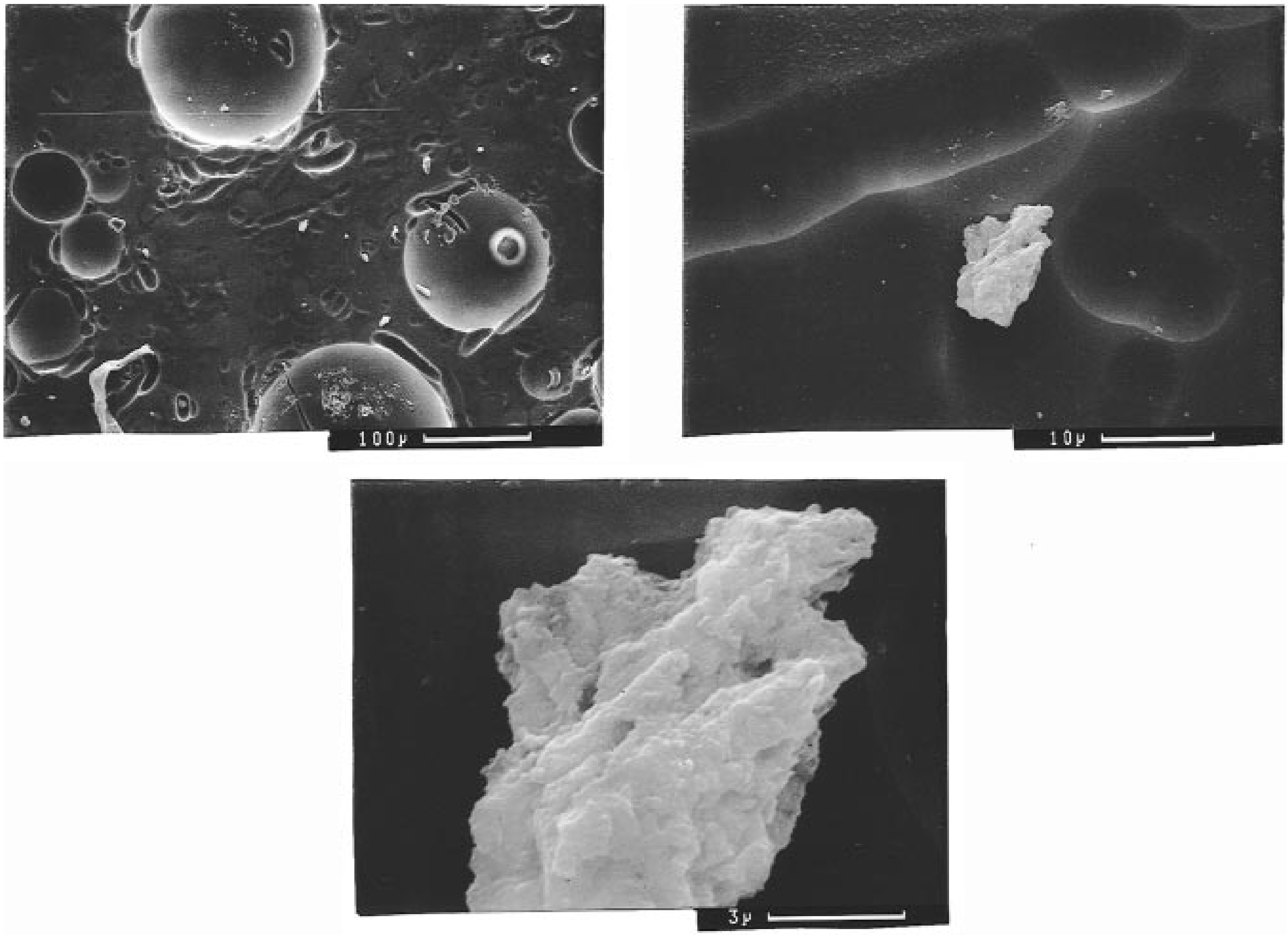

Figure 9. Micrographs showing the microstructure of a sintered sample of 1:1:6 composition at different magnifications.

glassy matrix. Thus an 8% increase in the amount of silica leads to crystallization of reduced amounts of BPO_4 phase in comparision to the 1:1:4 composition. This variation could alter the dielectric constant of the glass−ceramic.

Dielectric studies were conducted on several pressurelessly sintered 1:1:6 composition samples similar to the 1:1:4 composition. These results indicate an even lower average dielectric constant than those exhibited by the 1:1:4 composition. The results of these dielectric measurements are also shown in Table 2. The 1:1:6 composition samples exhibit an average dielectric constant of 3.77 and an average dissipation factor of 0.0008 at a frequency of 1 MHz. There is a noticeable decrease in dielectric constant in comparison to the 1:1:4 composition samples, and as was the case with the 1:1:4 composition, there is a small amount of visible porosity. Note that both compositions show similar amounts of reduced porosity in comparison to the corresponding MOSG gels. Therefore, the decrease in the dielectric constant is most likely due to the higher amount of the glassy phase, which has been reported to exhibit a lower dielectric constant ($\approx$3.8) than the crystalline BPO_4 phase; rather than the presence of pores or the loss of boron and phosphorous as soluble hydroxide species in the filtrate.[7,8] The reduced porosity observed in both compositions suggests that the MOSP process is a viable method for producing glass−ceramics in this system. In addition, the low values of dielectric constants ($<$5 at 1 MHz) obtained in both compositions suggest the potential of borophosphosilicate glass−ceramics as substrates for high-speed microelectronic packaging.

Conclusions

A new modified oxide sol-precipitation (MOSP) approach was used to synthesize borophosphosilicate glasses and glass−ceramics employing boron oxide and phosphorous pentoxide starting precursors. Two compositions corresponding to the oxide ratios; B_2O_3:P_2O_5:SiO_2 of 1:1:4 and 1:1:6 were synthesized. The powders were heat-treated up to 800 °C to crystallize boron phosphate. X-ray diffraction analysis indicates that the as-prepared powders of both compositions are amorphous. On the other hand, X-ray diffraction analysis conducted on the heat-treated samples reflect the presence of crystalline BPO_4. Sintered samples of 1:1:4 composition exhibited sharper and more intense BPO_4 peaks than those corresponding to 1:1:6 composition. This result is probably due to the presence of a larger volume fraction of the crystallized BPO_4 phase in the 1:1:4 samples. The crystallized gels were then sintered in air (1000 °C, 72 h) to obtain borophosphosilicate glass−ceramics. The increased ease of carbon removal from the as-prepared gel powders coupled with the reduced porosity seen in the pressurelessly sintered samples suggests the MOSP process to be quite attractive for processing oxide glasses and glass-ceramics in comparison to the MOSG process. The sintered specimens exhibited dielectric constants in the range 3.77−3.86 and dissipation factors in the range 0.0007−0.0008 at a frequency of 1 MHz, suggesting the excellent potential of these materials for use as substrates in electronic packaging.

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