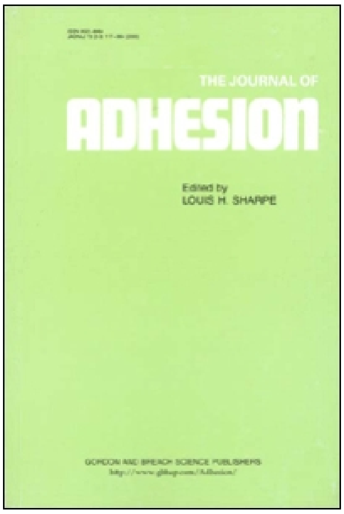

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Effect of MgO Addition on the Bondability and Interfacial Reaction between Dielectric and Glass-Ceramics for the Fabrication of Multi-Component Ceramic Substrates*

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Bondability and interfacial reaction between dielectric and insulator layers have been examined to obtain a basic understanding of bonding mechanisms. Lead-containing complex perovskite was used as a dielectric material. Two kinds of glass-ceramics were used as insulator material; lead borosilicate glass containing Al_2O_3 (insulator A) and the same containing Al_2O_3 and MgO (insulator B). Dielectric and insulator layers did not bond when insulator A was used. When insulator B was used, however, strong bonding was achieved between the two layers by firing the powder compacts at temperatures between 800° and 1000°C. Addition of MgO to lead borosilicate glass increased the thermal expansion coefficient to that of the dielectric and enhanced the formation of reaction layers, resulting in good bonding. Two reaction layers were identified. The main reaction products were enstatite and bredigite for one layer contacting the dielectric, and enstatite and a compound with the same diffraction pattern as that of faujasite for the other layers contacting insulator B.

KEY WORDS bonding of glass-ceramics and dielectric; insulators; interfacial reactions; interfacial bonding; interfacial microstructure; borosilicate glass; thermal expansion mismatch; microcircuits; large scale integration; LSI.

INTRODUCTION

Monolithic multi-component ceramic substrates contain resistors, capacitors and conductors (internal electrodes) for packaging large scale integrated circuits (LSI).[1,2] Ceramic substrates containing resistors and internal electrodes have been developed

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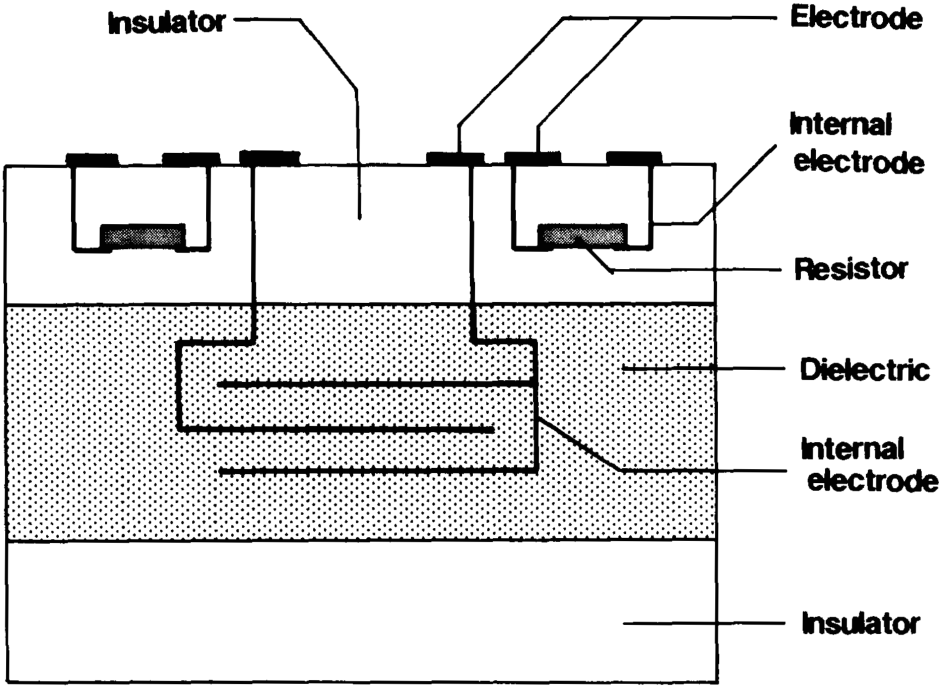


FIGURE 1 Model of monolithic multi-component ceramic substrates.

and used extensively.[3] It is desirable to include capacitors in the substrates to increase the packaging density. Figure 1 illustrates the basic concept of monolithic multi-component ceramic substrates.[2] These substrates are fabricated by firing composites composed of capacitor and insulator sheets made by microelectronic packaging technology.[3] Firing temperatures should be lower than 900°C in order to be able to use inexpensive wiring (conductor) materials. Lead-containing complex compounds with the perovskite structure[4,5] and glass-ceramics[6] are candidates for the capacitor (dielectric) and insulator materials, respectively. The bondability and reaction between different materials have to be controlled in order to fabricate substrates by co-firing of various materials.

Glasses containing Al_2O_3 as filler are normally used for insulator materials in ceramic substrates.[6] We found, however, that the bonding between dielectric and insulator (glass + Al_2O_3) layers was poor and that the addition of MgO to the glass enhanced the bondability. This paper deals with the effect of MgO addition on the bondability and interfacial reaction between dielectric and insulator layers. Dielectric and insulator materials used were complex perovskite and lead borosilicate glass containing Al_2O_3 and MgO, respectively.

EXPERIMENTAL PROCEDURE

A powder for the dielectric with the composition of $Pb(Mg_{1/2}W_{1/2})_{0.645}(Mn_{1/3}Nb_{2/3})_{0.01}Ti_{0.344}O_3$ was made by firing a mixture of PbO, MgO, WO_3, TiO_2, $MnCO_3$ and

Nb_2O_5 at 775°C for 4h. Two kinds of powders were used for the insulator: insulator A was a mixture of lead borosilicate glass (45 wt%) and Al_2O_3 (55%) and insulator B was a mixture of lead borosilicate glass (68.2%), Al_2O_3 (4.5%) and MgO (27.3%). The lead borosilicate glass contained SiO_2 (61.2 wt%), PbO (15.7%), B_2O_3 (6.4%), Al_2O_3 (5.5%), CaO (5.1%) and other oxides.

Dielectric and insulator sheets were made by tape casting of slurries containing powders, organic binder, plasticizer and solvent.[7] The thickness of the sheets was about 50 μm. The sheets were cut into small pads and multi-component compacts were made by stacking 15 sheets of each component and pressing under a pressure of 15 MPa. Single-component compacts were made by the same procedures. The compacts were slowly heated to 450°C in O_2 atmosphere, to burn out the binder and plasticizer, and then fired at various temperatures for various durations.

The sintered compacts were cut and polished to examine the structure of the interfacial region. Microstructure was observed with a scanning electron microscope (SEM), the distribution of elements was measured by energy dispersion X-ray (EDX) analysis and the phases present were identified by X-ray diffraction (XRD) analysis. Thermal expansion behavior was examined with a dilatometer.

RESULTS AND DISCUSSION

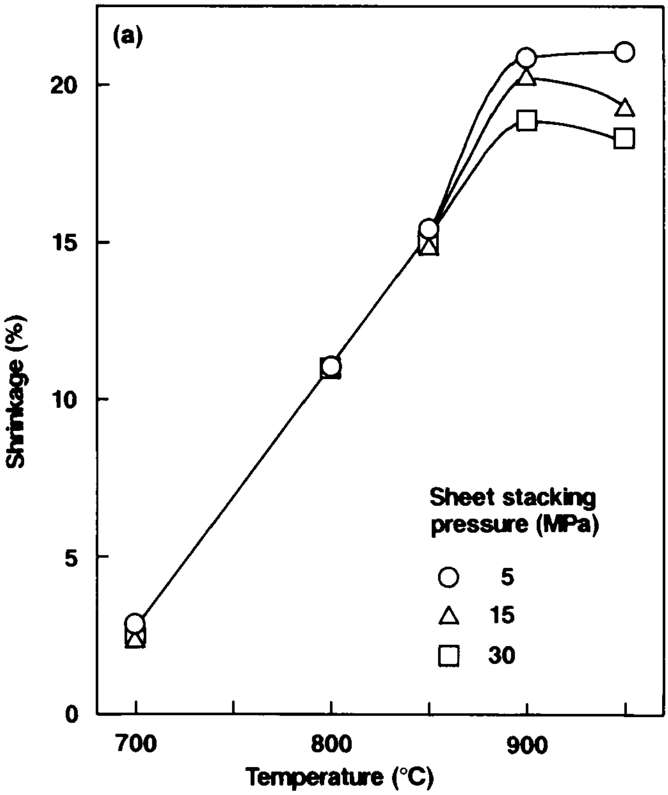
Bondability between Dielectric and Insulator Layers

Strong bonding between dielectric and insulator layers was achieved by firing the compact at a temperature between 800° and 1000°C when insulator B was used, whereas the two layers did not bond when insulator A was used.

Figure 2 shows the effect of sheet stacking pressure on the shrinkage of single-component compacts fired at various temperatures for 1h. The compaction pressure gave a small effect on shrinkage for the dielectric fired at temperatures up to 850°C. Above 900°C, large pressure resulted in small shrinkage. The shrinkage of insulator B was dependent on the compaction pressure above 800°C. The difference in packing characteristics of powder particles in "green" sheets is responsible for the different effects of compaction pressure. The temperature dependence of shrinkage was also different for the dielectric and insulator B. The sintering of the dielectric proceeds in the solid state, whereas that of insulator B proceeds in the presence of a vitreous glassy phase. The difference in the densification mechanism is responsible for the different dependence of shrinkage on the firing temperature.

The maximum shrinkage of the dielectric was about 20% at 900°C, whereas that of insulator B was about 15% between 800° and 950°C. A compaction pressure of 15 MPa and firing temperature of 850°C were chosen in further experiments. Under these conditions, the same shrinkage (about 15%) was obtained for the dielectric and insulator.[8] The shrinkage of insulator A was also about 15%.

From the data shown in Figure 2, a large mismatch in shrinkage is expected between the dielectric and insulator B during the heating of two-component compacts. The fact that insulator B achieved good bonding to the dielectric suggests that the mismatch in shrinkage during heating is not a factor which determines the bondability. Probably, the vitreous glassy phase relaxes the stress caused by the different shrinkage.



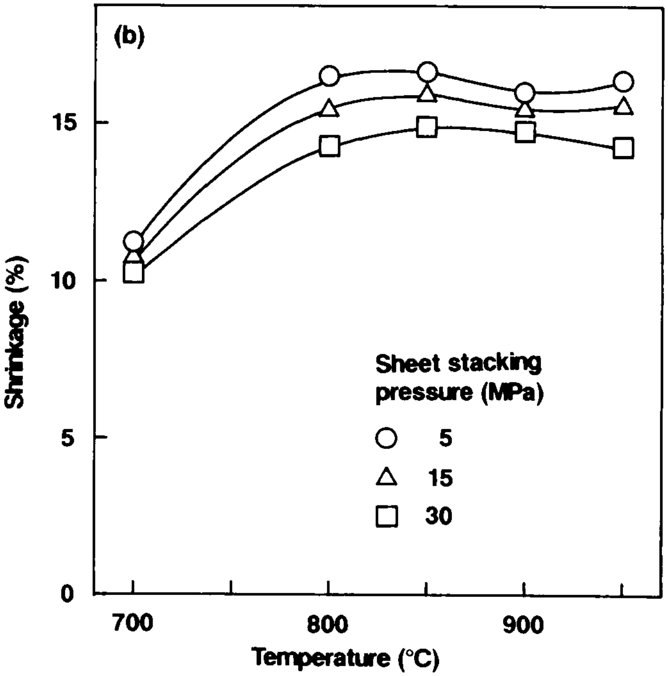


FIGURE 2 Shrinkages of "green" single-component compacts of (a) dielectric and (b) insulator B fired at various temperatures for 1h.

Figure 3 shows the thermal expansion behavior of sintered, single-component compacts fired at 850°C for 1h. The mismatch in the thermal expansion coefficient between sintered dielectric and insulator compacts was larger for insulator A than for insulator B. No crystalline phase was detected by XRD analysis in the glass compact fired at 850°C for 1h. When the single-component insulators were fired at 850°C for 1h, Al_2O_3 and anorthite ($CaAl_2Si_2O_8$) were present in insulator A and MgO, forsterite (Mg_2SiO_4) and augite ($Ca(Mg,Al)(Si,Al)_2O_6$) were present in insulator B (Al_2O_3 and MgO were the major crystalline phases for insulators A and B, respectively). Figure 4 shows the thermal expansion behavior of Al_2O_3, MgO and Mg_2SiO_4. Magnesia and Mg_2SiO_4 have larger thermal expansion coefficients than Al_2O_3. The thermal expansion coefficient of insulator B being larger than that of insulator A is caused by the presence of MgO and Mg_2SiO_4.

The large mismatch in the thermal expansion coefficient is partly responsible for poor bondability between the dielectric and insulator A layers; stresses develop during cooling of the sintered two-component compact. This stress is not relaxed and leads to cleavage, because the viscosity of the vitreous glassy phase is large at low temperatures and no relaxation is expected.

The formation of reaction layers is another factor influencing the bondability.[9] Only a layer into which Pb diffused formed at the interfacial region for insulator A,

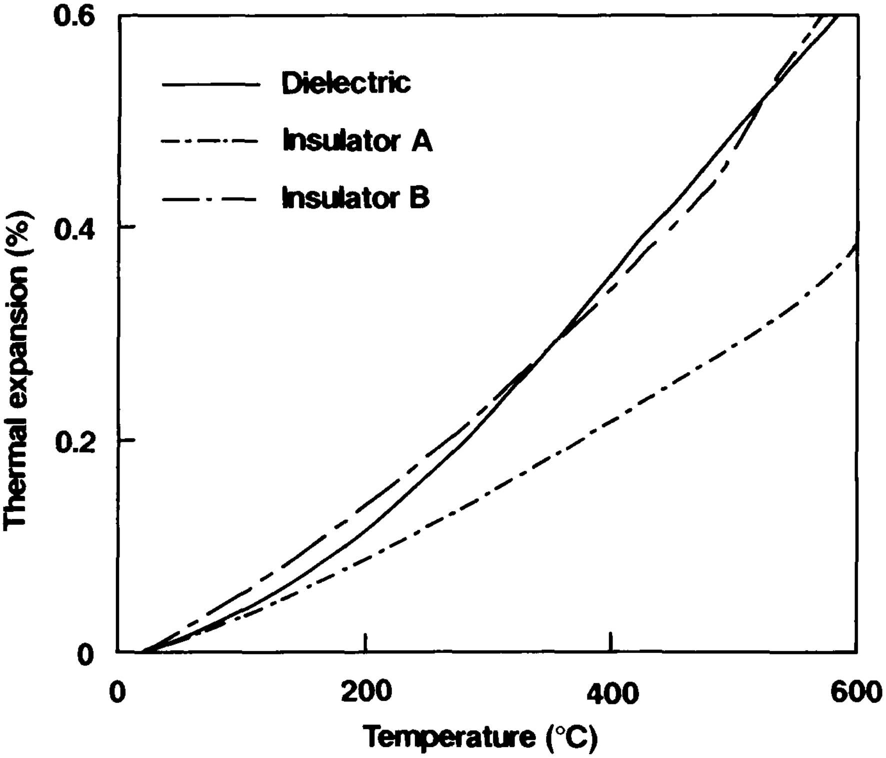


FIGURE 3 Thermal expansion characteristics of sintered single-component compacts.

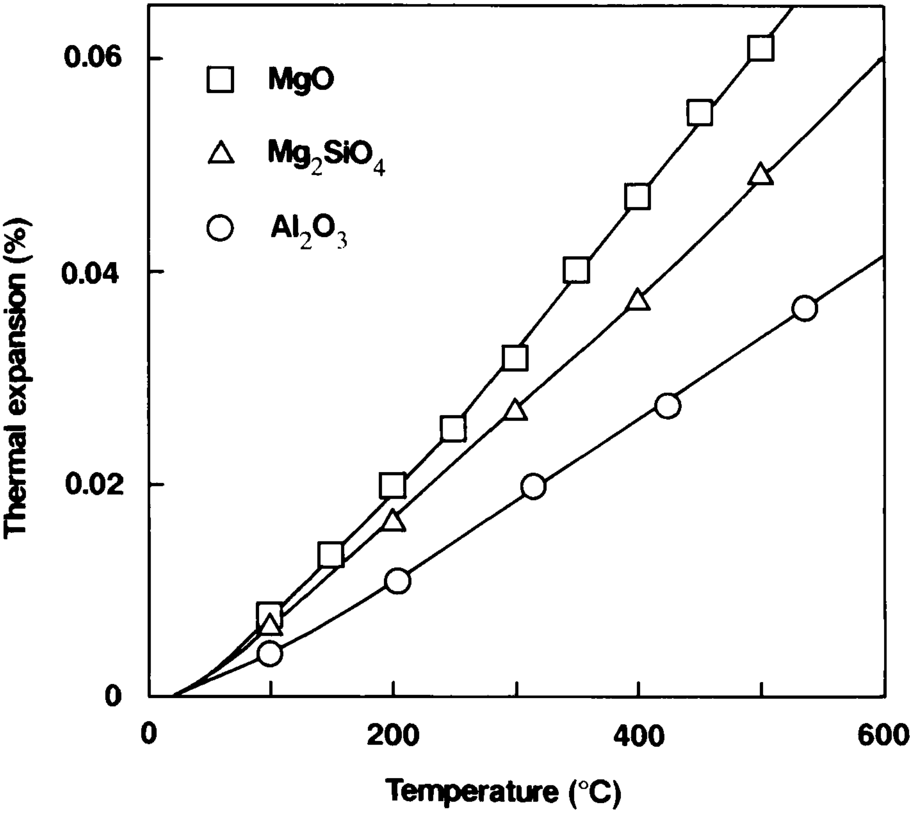


FIGURE 4 Thermal expansion characteristics of alumina, magnesia and forsterite.

whereas reaction layers with various product phases formed for insulator B. Figure 5 shows the microstructures of dielectric and insulator A layers at the interfacial region of the compact fired at 850°C for 1h. No microstructural change was observed in the dielectric layer, whereas a bright region was observed in the insulator layer. Accumulation of Pb in this region was confirmed by EDX analysis. Figure 6 shows the microstructure of reaction layers at the interfacial region in the dielectric-insulator B sample fired at 850°C for 1h. Two reaction layers were present between the dielectric and insulator layers. We designate them as Reaction Layers 1 and 2; the former is in contact with the dielectric layer and the latter with the insulator layer. The original interface was located in Reaction Layer 1.

Several compounds formed on addition of Al_2O_3 or MgO into the glass, as described above. The formation of different crystalline phases resulted in the difference in the composition of the glass phase in insulators A and B, leading to different characteristics of reaction with the dielectric layer. The formation of new compounds at the interface improves bondability.[9] Thus, the addition of MgO to the glass improved thermal expansion mismatch between the dielectric and insulator layers and resulted in the reaction products which formed at the interface, leading to better bondability.

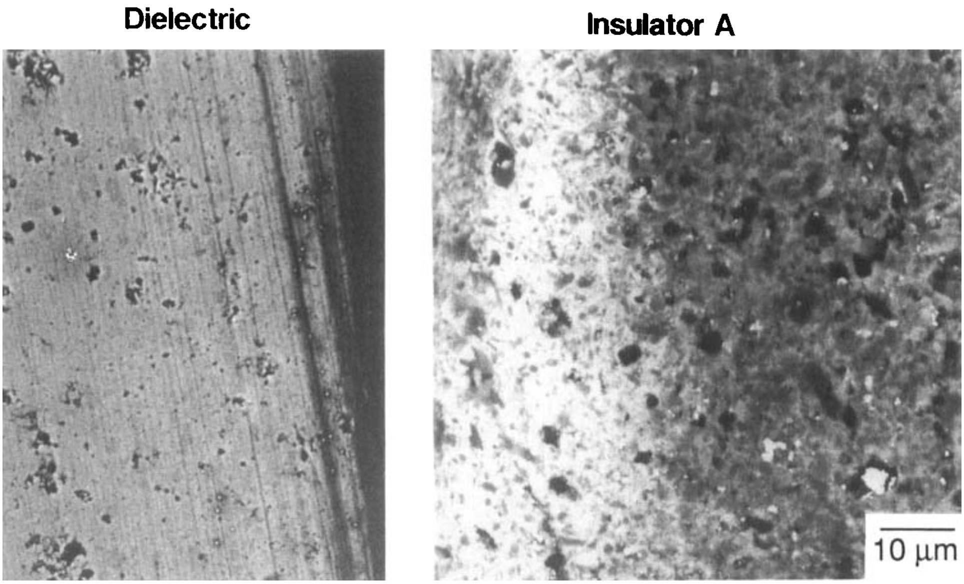


FIGURE 5 Microstructures of dielectric and insulator A near the interface in the dielectric-insulator A compact fired at 850°C for 1h. This sample was debonded after cooling to room temperature.

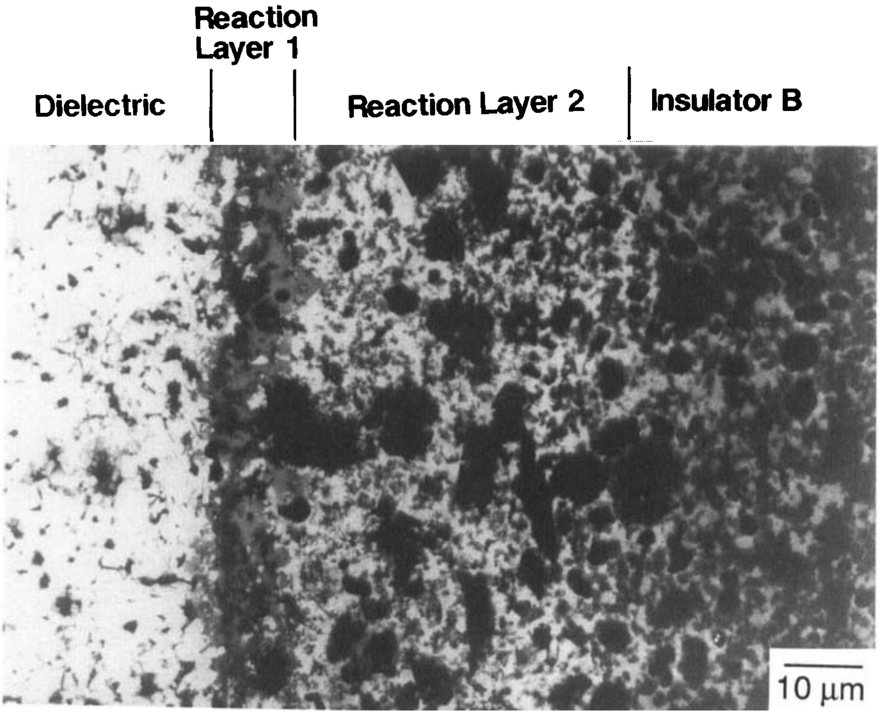


FIGURE 6 Microstructure of the interfacial region of the dielectric-insulator B compact fired at 850°C for 1h.

Reaction Products between Dielectric and Insulator B Layers

This section deals with the reaction products formed in the dielectric-insulator B compact fired at 850°C for 1h.

The distribution of elements was measured by EDX analysis (Fig. 7). The concentration of lead, which is one of the components of the dielectric and insulator materials, was low in Reaction Layer 1. Silicon and Ca, not contained in the dielectric, were present in Reaction Layers 1 and 2 and also in the dielectric layer in contact with Reaction Layer 1. No obvious accumulation or depression was observed for Mg. The dielectric layer in contact with Reaction Layer 1 was enriched with W. This result indicates that Reaction Layer 1 was composed mainly of Mg, Ca and Si and contained a smaller amount of Pb than the other layers. Reaction Layer 2 contained Pb, Mg, Ca and Si.

Figures 8 and 9 show the microstructures of Reaction Layers 1 and 2, respectively, on a larger scale. The microstructures of Reaction Layers 1 and 2 were complicated. Figure 8 indicates the presence of needle-like grains in the dielectric layer in contact with Reaction Layer 1. These needle-like grains were also present in Reaction Layer 1. A continuous layer was the main product in Reaction Layer 1. Reaction Layer 2 was composed of large equiaxed grains (black), rod-like grains (gray), and matrix

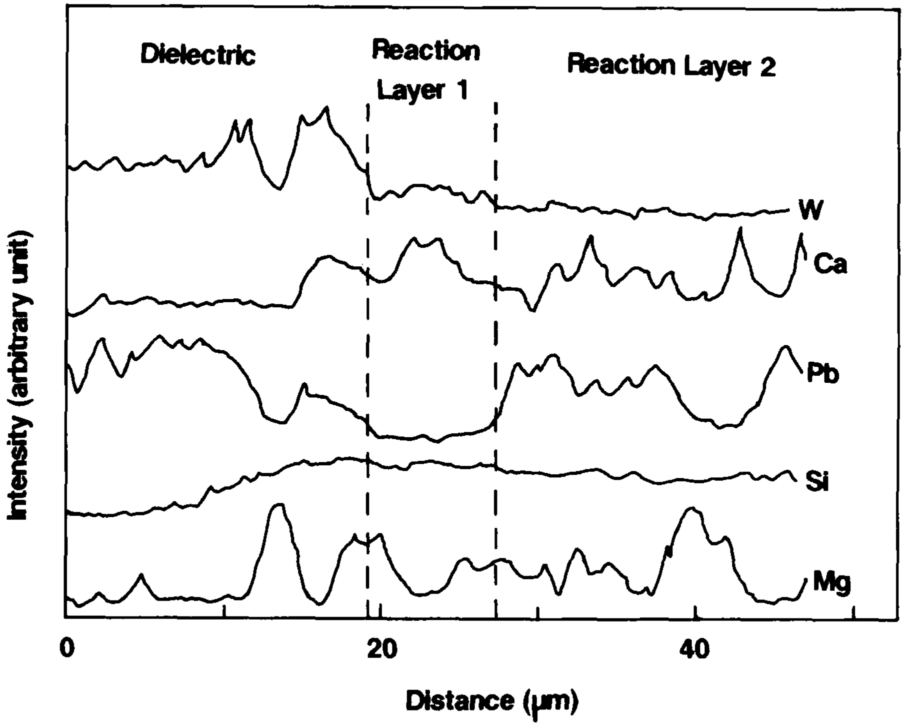


FIGURE 7 Distribution of elements at the interfacial region of the dielectric-insulator B compact fired at 850°C for 1h.

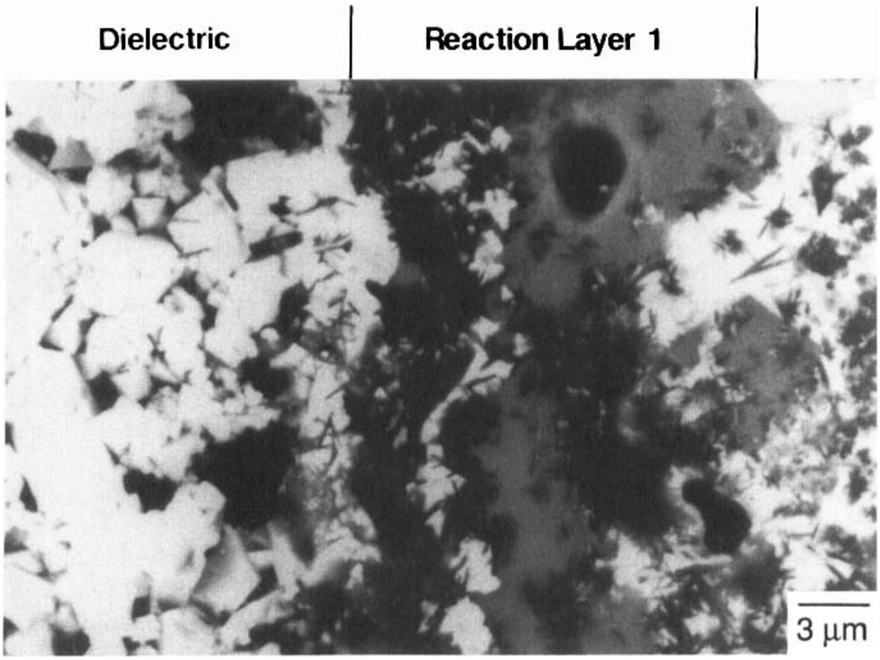


FIGURE 8 Microstructure of Reaction Layer 1 in the sample shown in Fig. 6.

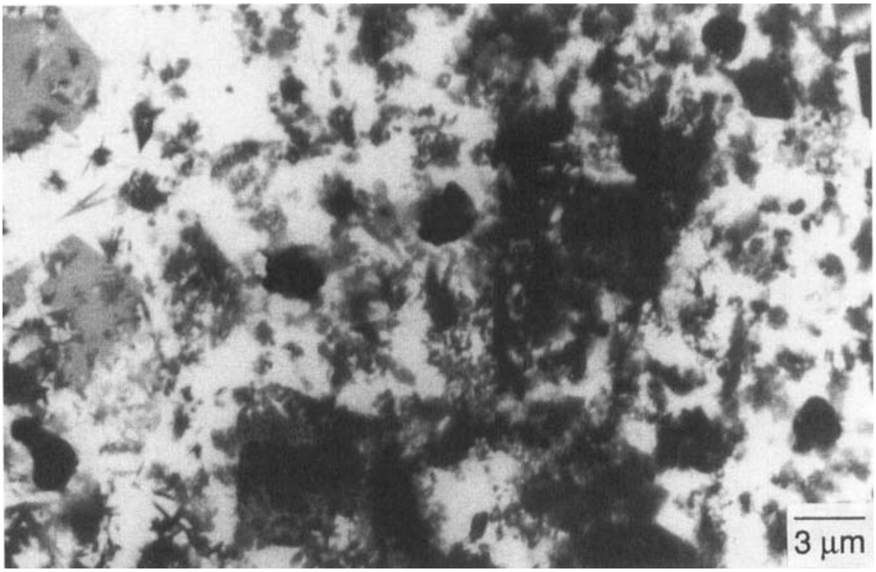


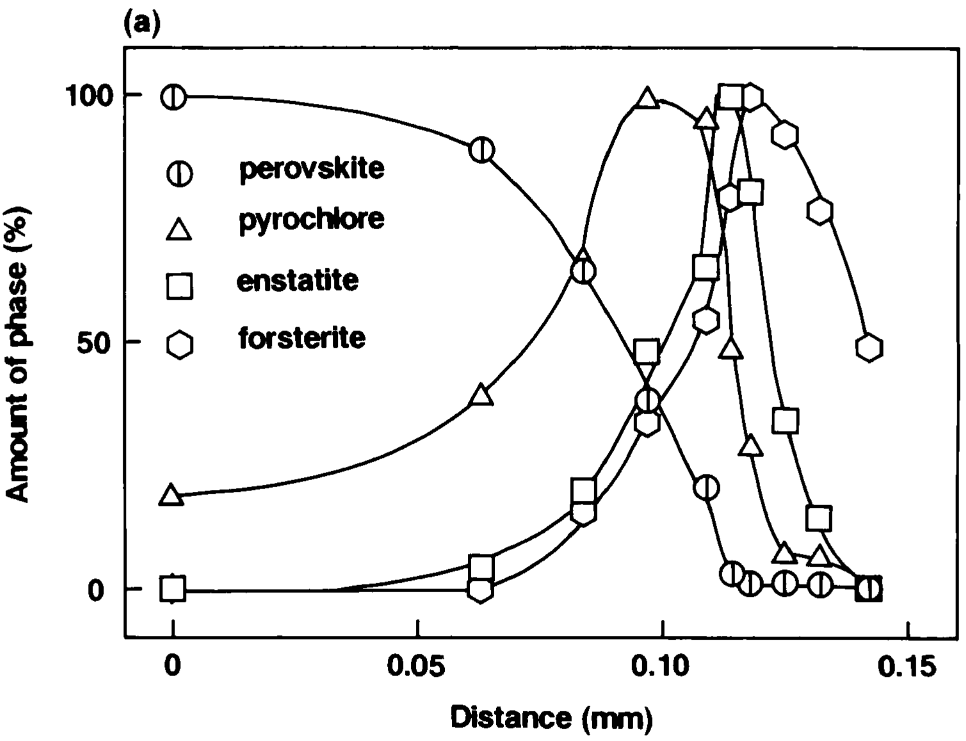
FIGURE 9 Microstructure of Reaction Layer 2 in the sample shown in Fig. 6.

(white) (Fig. 9). Large equiaxed grains and gray rod-like grains were composed of light elements (probably Mg, Ca and Si). The matrix was enriched with Pb.

The crystalline phases in the reaction layers were examined by XRD analysis. The sample was polished parallel to the interface to reveal the reaction layer and then the phases present were identified. The measurement was repeated on successive grinding. Figure 10 shows the percentages of the different phases as a function of distance. The amounts were normalized with respect to the maximum amount of each phase.

Perovskite and pyrochlore were major phases in the dielectric layer near the interface and the amount of pyrochlore increased near the interface. The diffusion of Pb from the dielectric layer into the insulator layer decreased the concentration of Pb in the dielectric layer, resulting in the formation of pyrochlore. Enstatite ($MgSiO_3$) and forsterite (Mg_2SiO_4) were also observed in this region. Silica migrated from the insulator layer into the dielectric layer and reacted with MgO, one of the constituents of complex perovskite, to form $MgSiO_3$ and Mg_2SiO_4.

Figure 10 indicates that the major product phases are enstatite and bredigite ($(CaMg)_2SiO_4$) in Reaction Layer 1 and forsterite and a compound with the same diffraction pattern as that of faujasite ($Na_2Al_2Si_4O_{12}$ $8H_2O$) in Reaction Layer 2. The faujasite-like compound might be a silicate containing Pb and Ca, as judged from the results of EDX analysis. This result indicates that the needle-like grains



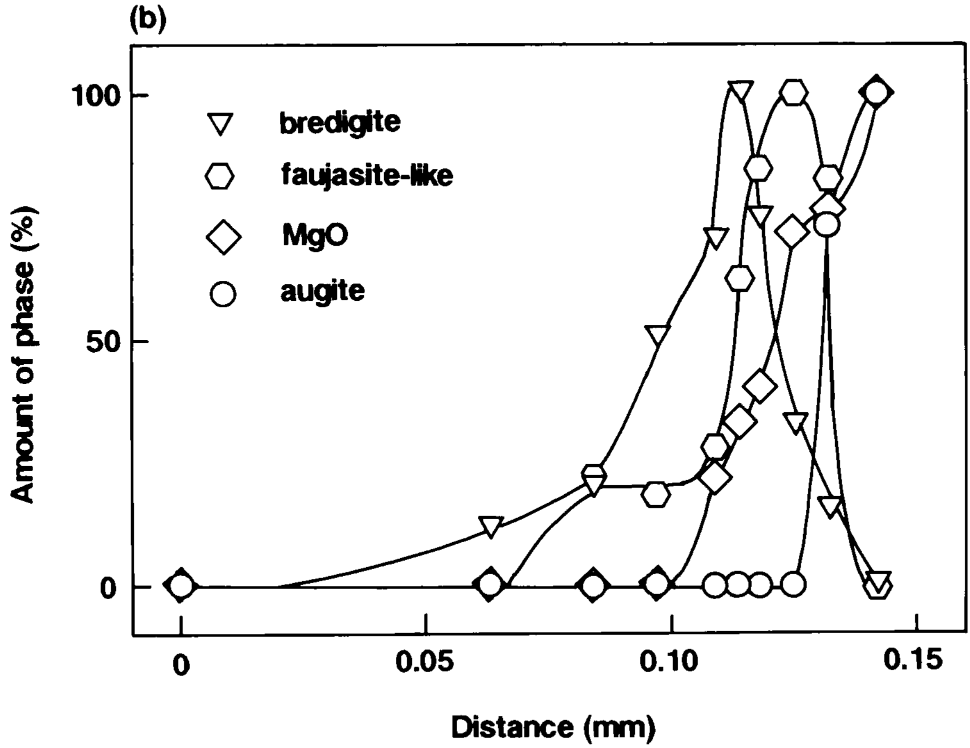


FIGURE 10 Amount of product phases as a function of distance for the dielectric-insulator B compact fired at 850°C for 1h.

and continuous layer in Reaction Layer 1 are enstatite and bredigite, respectively. The identification of the crystalline phases in Reaction Layer 2 is difficult. Probably, the equiaxed and rod-like grains are forsterite and the faujasite-like compound, respectively. The matrix is the glass phase.

CONCLUSIONS

Poor bondability between the dielectric and insulator A was explained by the large mismatch in the thermal expansion coefficient and the lack of a reaction layer. Addition of MgO to lead borosilicate glass decreased the thermal expansion mismatch with the dielectric and enhanced the formation of reaction layers, resulting in good bonding between dielectric and insulator layers. Diffusion of Pb from the dielectric layer to the insulator layer and that of Si in the reverse direction resulted in reaction layers with complicated microstructures. Crystalline phases in the reaction layers were mainly silicates, which had an anchoring effect between the dielectric and insulator layers.

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