Microstructure of mullite ceramics used for substrate and packaging applications

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The objective of this investigation was to explain the variation in dielectric constants of mullite ceramics prepared with 25% excess silica under a variety of conditions as described in an earlier study. Different starting materials, mullite–silica (M–S) and alumina–silica (A–S), different particle sizes (fine or coarse) and different firing times and temperatures were used. Dielectric constants measured for the alumina–silica system at 1550 °C at different times, showed an initial reduction followed by an increase on further heating. The dielectric constants of other systems increased with increase in heat-treatment time at the different heat-treatment temperatures. From the study of microstructures using transmission electron microscopy and energy dispersive X-ray spectroscopy, it was shown that the initial decrease in dielectric constant on heating the alumina–silica system was because alumina, a phase with a higher dielectric constant was being replaced by mullite, a phase with a lower dielectric constant. On completion of this reaction, the intergranular silica was absorbed by mullite thereby leading to an increase in the dielectric constant. It was then shown that whenever phases with a lower dielectric constant exist, the dielectric constant of the system as a whole is lower.

1. Introduction

Ceramics have played an important role in circuit packaging since the 1950s due to their unique combination of mechanical, dielectric, physical and chemical properties. Ceramics are used in high-frequency circuits, such as in the thermal conduction module (TCM), which provides the high-density wiring needed in large-scale computers. Alumina is currently used as the substrate material. However, the speed with which the signals pass through the substrate is controlled by the dielectric constant of the media through which it passes. An important parameter that should be kept as short as possible is the signal transmission delay time given by

$$t_d = (\varepsilon^* s)^{1/2}/c \qquad (1)$$

where s is the signal path length, c is the velocity of light and ε is the dielectric constant of the material [1–3]. Mullite, with $\varepsilon = 6.7$, has 21% smaller t_d than alumina, which has $\varepsilon = 9.8$, and is being considered as a replacement material for alumina in high-performance (speed) circuitry.

There are other properties of mullite that are useful for packaging. Mullite multilayer ceramic technology is expected to be used increasingly instead of the alumina substrate currently in use in high-performance midrange computers [4]. Solder connection, referred to as controlled chip connection, between a chip and

the substrate is being used more because of its advantages in providing the number of connections, as well as the low inductance of the connections. This connection requires a good thermal-expansion match between silicon and the substrate for current substrate systems, and mullite–alumina–silica system has a lower thermal-expansion mismatch than alumina [4].

The composition of the ceramic chosen for this study was 75 vol % mullite and 25 vol % silica to combine the high strength of mullite with the low dielectric constant of silica ($\varepsilon = 4$). This study focused on the change in microstructure of the ceramics on varying the firing times and temperatures of the various raw powder materials used, and was used to explain the variation in dielectric properties of the materials which were previously studied [5].

2. Experimental procedure

Powder raw materials included in this study were relatively fine- and coarse-grained silica, fine-grained alumina, and coarse-grained mullite. Phase equilibria studies [6–12] indicate some solid solubility of silica with mullite, and existence of a eutectic at 1590 °C. Thus samples near equilibrium reacted at temperatures above 1590 °C will undergo liquid-phase reaction, and samples reacted at temperatures below this undergo a solid state reaction. The firing temperatures

used were 1500, 1550 and 1630 °C and the times varied from 12–44 h.

The samples were prepared using a starting composition equivalent to 75 vol % mullite and 25 vol % silica [5]. The compositions are denoted by various powder starting materials: alumina was denoted by A, silica by S, and mullite by M; c and f were used to denote the grain size (coarse or fine). So, a ceramic made with fine alumina grains and coarse silica grains can be denoted by Af–Sc, and if fine mullite was used instead of alumina, it can be denoted by Mf–Sc. Processing and measurements of dielectric constants and densities at different heat-treatment times and temperatures were done in the earlier study [5].

TEM samples were prepared by making thin sections using a diamond blade, followed by drilling 3 mm discs using a slurry mill, grinding it using silicon carbide paper (grit size 400–2400) and finally ion milling to obtain thin sections. The samples were coated with carbon to avoid problems of charging during the TEM study.

The samples were studied using a TEM (Philips 420) which had an EDS (EDAX) unit attached to it. Because aluminium and silicon have their K_α peaks close together, the peaks could not be resolved for mullite samples. However, from the shapes of the peaks and the positions of the peak maxima, it was possible to comment on the approximate mullite composition (for example, if one sample was silica-rich compared to the other), and if the peaks corresponded to aluminium or silicon, if unreacted grains of alumina or silica were present. The existence of these phases was also confirmed by indexing the diffraction patterns. Silica was always present as a glassy phase, and this was confirmed by the absence of phase contrast in the silica grains on tilting the sample in the TEM.

3. Results

The study of microstructures was based on an earlier study [5] where the dielectric constants of various mullite samples were measured as a function of density for different heat-treatment times and temperatures. The results are categorized based on the starting material composition, i.e. whether it belonged to the alumina–silica (A–S) system or the mullite–silica (M–S) system, and whether the starting powder particle size was fine (f) or coarse (c).

The Af–Sf samples heated at 1500 °C for 12 h had a dielectric constant, ε, value of 6.53 and a density of 66.8%. The microstructure showed mullite particles 1.2–2 μm in size. Silica was observed as a glassy phase between the grains of mullite and its thickness was usually 0.1–0.2 μm, though it was as much as 0.6 μm at certain points. Considerable porosity was observed. There were also small amounts of crystalline alumina particles found. Fig. 1a from the Af–Sf sample sintered at 1500 °C for 12 h shows a bright-field image from an unreacted alumina grain which is indicated with an arrow, with the double arrow showing an unreacted silica grain. Fig. 1b and c show the EDS peaks from the alumina and the silica grain, respectively.
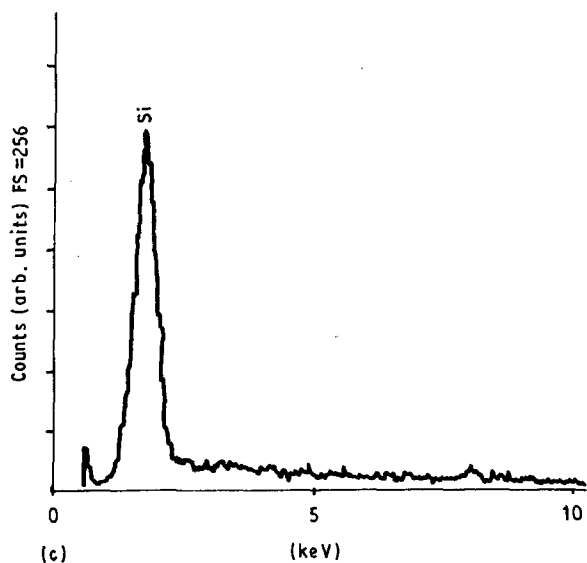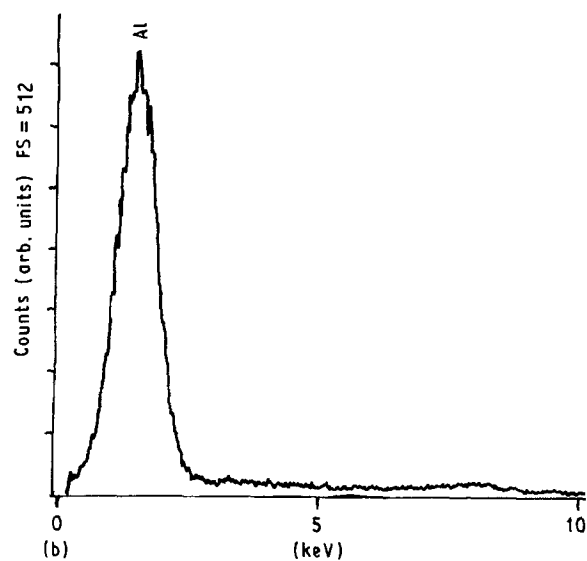

Figure 1 (a) Bright-field from Af–Sf sample fired at 1500 °C for 12 h. Single arrow points towards the alumina grain and the double arrows show an unreacted silica particle. (b) An EDS peak from the alumina particle and (c) from the silica particle.

For the Af–Sf system heat treated at 1550 °C for 12 h, the ε value was found to be 6.79, and the density was 71.8%. The microstructure showed unreacted silica particles which were 1.5 μm diameter. In general, silica was present as a glassy intergranular phase of thickness 0.3–0.5 μm. There was a lot of unreacted silica in the specimen. The mullite grain size varied from 0.8–2.5 μm.

For Af–Sf samples that were heated at the same temperature (1550 °C) for 44 h, the ε value decreased to 6.23, and the density increased to 82.2%. The microstructure showed that the silica thickness at the grain boundary was less than 0.02 μm. The mullite grains were 1.5–3 μm in size, and several grains of size 0.1–0.5 μm were observed inside these grains.

The Af–Sf samples that were heated at 1630 °C for 24 h showed a lower ε value of 5.37, and a higher density of 86.9%. The silica thickness was in parts as low as 0.03 μm, and in many regions, there was no intergranular silica at all. In a few regions, it went up to 0.4 μm, and these regions were at the intersection of a few mullite grains. The mullite grains were about 2 μm in size and the particle size was uniform.

The Af–Sc sample heated at 1550 °C for 24 h showed a density of 86.3% and an ε value of 5.33. The grain size of mullite was between 0.9 and 1.6 μm. Silica was observed only at the grain boundaries and was 0.1 μm thick at most grain boundaries and was never more than 0.2 μm thick. Alumina particles of 0.1 μm size were observed. Fig. 2 obtained from Af–Sc samples heat treated at 1550 °C for 24 h shows the presence of intergranular silica between grains of mullite.

The Af–Sc sample heat treated further at the same temperature (1550 °C) to 44 h had an ε value of 7.35 and a density of 88.3%. The mullite grains were around 1.5 μm in size, and silica was present as a thin layer around mullite grains, but there were also regions where no such silica was present. This is seen clearly in Fig. 3, with the arrows pointing towards the unreacted silica.

The Mc–Sc sample heat treated at 1550 °C for 12 h had an ε value of 3.870 and a density of 88.3%. The EDS spectrum from the mullite grain for this sample showed a distinctly higher silica peak when compared to the other alumina–silica samples. The mullite grains were 0.7–1 μm in size. Silica was not usually present as a continuous intergranular phase, but was present at the point of intersection of two grains or around pores. The thickness of the silica varied from 0.02–0.1 μm, but in some regions was 0.7 μm thick. From the study of the diffraction patterns for these samples, it was noted that the mullite lattice was slightly distorted and this was probably due to the absorption of silica into the lattice.

4. Discussion

The basis for the discussion presented here is that whenever phases with lower dielectric constant were present, the dielectric constant of the system as a whole was lower. This is not necessarily obvious, as in a system with as many phases as this one, the dielectric constant may increase or decrease depending on whether the capacitances associated with the dielectric constant of each phase adds up in series or parallel and the morphology of the phases. The arguments presented here explain the dielectric data obtained in a consistent manner, and can be assumed to be correct because all of the phases, mullite, silica and alumina, are insulating. Also all the phases present are
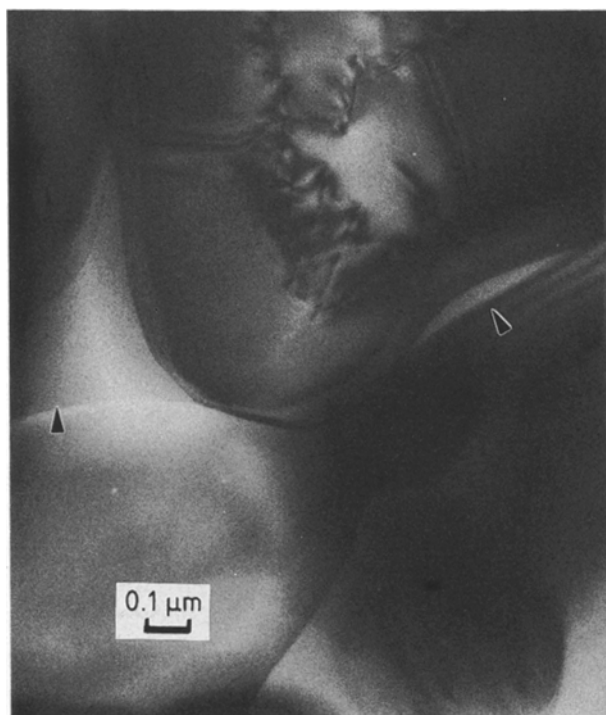

Figure 2 Microstructure of mullite grains from an Af–Sc sample fired at 1550 °C for 12 h. Arrows point towards regions of intergranular silica.

Figure 3 Microstructure of mullite grains from Af–Sc sample fired at 1550 °C for 44 h. Arrows point towards unreacted silica around pores. Notice the absence of intergranular silica.

equiaxed. The phases present, in increasing order of dielectric constant values, are silica ($\varepsilon = 4$), mullite ($\varepsilon = 8$) and alumina ($\varepsilon = 9.8$). Porosity also plays a role in controlling the dielectric constant, and its dielectric constant was assumed to be that of air ($\varepsilon = 1$).

Considered first were the Mc–Sc samples. They showed an increase in dielectric constant with increasing heat-treatment time (Fig. 4 [5]). The microstructure showed a decrease in silica and porosity, the silica being absorbed into the mullite matrix. Because the phases with a lower dielectric constant were less abundant, the dielectric constant of the system increased.

Considered next were the Af–Sf and Af–Sc systems. The samples treated at 1550 °C showed a rapid decrease in dielectric constant on firing for 12–24 h (Figs 5 and 6 [5]). Most of the alumina had reacted with silica to form the lower dielectric constant phase, mullite, therefore lowering the dielectric constant of the system as a whole, even though there was a decrease in porosity. On further treatment at the same temperature, the dielectric constant increased because of absorption of silica into the mullite phase. In the
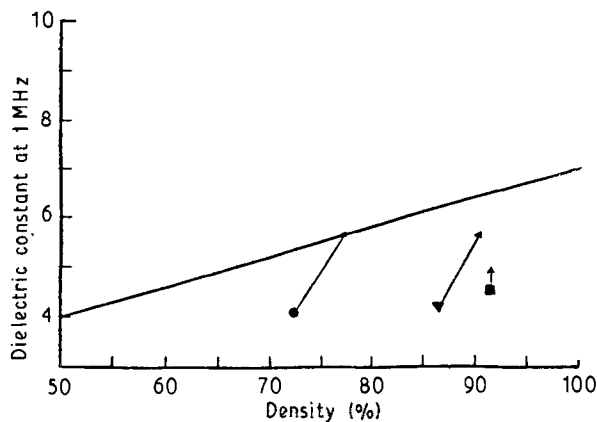

Figure 4 Dielectric constant as a function of per cent theoretical density for the coarse mullite and the coarse silica system. The solid line represents the parallel rule of mixtures with a 100% density value of $\varepsilon = 7$ (assuming mullite is 8 and silica is 4) and open pore space value of 1. ($\bullet$, $\blacktriangledown$, $\blacksquare$) are the 12 h data and the connected arrow heads ($\blacktriangle$) are the respective 24 h data [5]. ($\bullet$) 1500 °C, ($\blacktriangledown$) 1550 °C, ($\blacksquare$) 1630 °C.
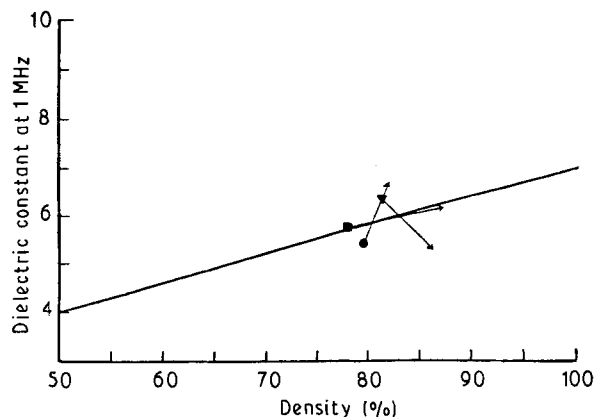

Figure 5 Dielectric constant as a function of per cent theoretical density for the fine alumina and coarse silica (Af–Sc) system [5]. For key, see Fig. 4.
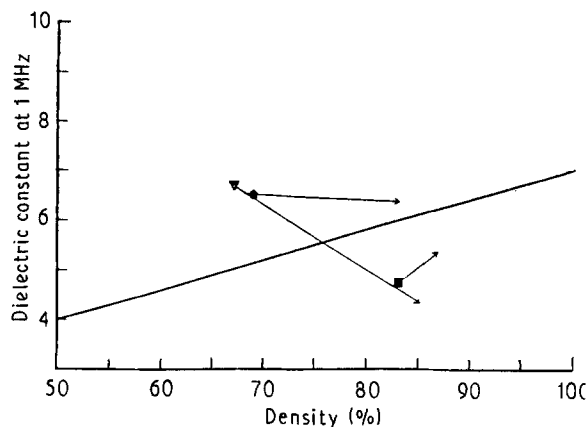

Figure 6 Dielectric constant as a function of per cent theoretical density for the fine alumina and fine silica (Af–Sf) system [5]. For key, see Fig. 4.

Af–Sf system fired at 1500 °C, the reaction between alumina and silica was probably slower than when heat treated at 1550 °C, and so the decrease in dielectric constant was lower. In the Af–Sc system, the reaction was so slow at 1500 °C that the dielectric constant increased due to a decrease in porosity. The Af–Sf samples heated at 1630 °C to 12 h, all alumina had reacted with silica to form mullite, and so on further heating, the absorption of silica into mullite caused an increase in dielectric constant, as shown in Fig. 6.

Acknowledgements

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