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Preparation, microstructural development and dielectric properties of $Pb(Mg_{1/3}Nb_{2/3})O_3$–$Pb(Ti_xZr_{1-x})O_3$ multilayer ceramic capacitors

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Multilayer ceramic capacitors based on PMN–PZT solid solutions have been prepared using a 70% Ag–30% Pd alloy as internal electrode. Some interaction of the electrode–dielectric with Ag^+ diffusion into the dielectric was observed. The Ag^+ diffusion influenced the normal microstructural development present in the PMN–PZT ceramics. In spite of this, the dielectric behaviour of a five active layers capacitor sintered at 1050 °C for 2 h in air showed a capacitance of 120 nF, an effective dielectric constant maximum of ~200 000 and dielectric losses of about 3% near room temperature and 1 kHz.

1. Introduction

The use of modified $BaTiO_3$ powders for the fabrication of multilayer capacitors (MLCs) [1–3] is widely recognized. However, the firing temperature of such MLCs (≥1300 °C) implies the use of high melting point internal electrodes, such as Ag/Pd 30/70 alloys or even palladium metal, in the metal–ceramic co-firing step of its fabrication process. Thus, not only is a considerable increase of the final MLC cost incurred, but also, as a consequence of the different sintering characteristics of both the ceramic and the internal electrodes, some microstructure defects occur, such as (a) delaminations, (b) interaction electrodes/ceramics, and (c) microstructure heterogeneities. As a consequence of this, the performances of the MLC could be devalued.

Many attempts have been made to avoid the above-mentioned problems; the most important of these are (a) lowering the firing temperature of the already known dielectric materials, (b) searching for low-firing dielectric ceramics, and (c) modifying the present MLC fabrication method leading to the elimination of the metal–ceramic co-firing step by using the metal impregnation method [4]. Any contribution to the above research areas will make the use of higher silver content alloys or base metals as internal electrodes possible and, in that sense, will reduce the final MLC cost without significantly decreasing their performances.

Of the low sintering dielectric ceramics, the more promising ones are those having the perovskite structure of the type $Pb(AB)O_3$ in which the A sites are occupied by cations such as Mg^{2+}, Fe^{3+}, Ni^{2+}, Zn^{2+}, and the B sites by Ta^{5+}, Nb^{5+}, and W^{6+}. These ceramic materials can be sintered at temperatures as low as 1000 °C, exhibiting a dielectric constant higher than 10 000 and dielectric losses lower than 3%. However, these perovskite-type ceramics, particularly in the case of the $Pb(Mg_{1/3}Nb_{2/3})O_3$ (PMN) compound, are difficult to obtain in the single-phase state [5–7], because in the majority of the cases, a second pyrochlore phase is present which, owing to its poor electric properties, degrades the performances of the PMN ceramics.

In the case of high-performance MLC dielectrics, which are very sensitive to the microstructural changes in the bulk ceramic, the purity, compositional homogeneity, and grain-size uniformity must be carefully controlled. In that way MLC dielectrics with improved electrical properties could be obtained.

The aim of the present work was to evaluate both the microstructural and electrical properties of an MLC dielectric prepared from a homogeneous PMN powder containing 10 mol % $PbTiO_3$–$PbZrO_3$ as a perovskite-phase stabilizer agent, using 70% Ag/30% Pd alloys as internal electrodes.

2. Experimental procedure

The 0.9PMN–0.1PZT powder preparation has been described in detail elsewhere [8]. Slurries for tape casting were made by a two-step milling process. In the first one, PMN–PZT powder was mixed with the solvent (an azeotropic mixture of methyl ethyl ketone and ethanol) and the dispersant (ester phosphate), and then ball milled for 2 h with zirconia media. After milling the plasticizer (benzyl butyl phtalate + polyethylene glycol) and the binder (polyvinyl butyral) were added, and again ball-milled for 7 h. The final powder/solvent/dispersant/plasticizer/binder slurry composition was 59/30/0.2/1.80/8.90 wt %. A laboratory-tape caster with a doctor blade was used and the slurry was spread on a flat glass surface at a rate of 1.6 $cm\,s^{-1}$, which produced a green-tape thickness of about 120 μm. The green tapes were cut into smaller sections of about $5 \times 5\ cm^2$, and then 70% Ag/30% Pd

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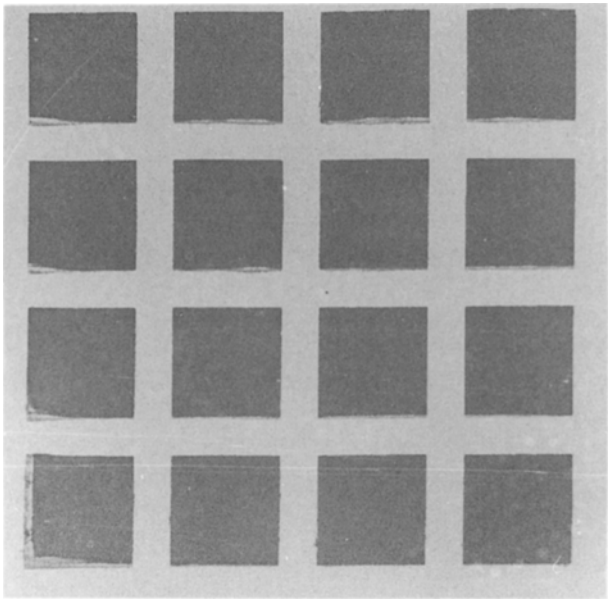


Figure 1 Fabrication and internal electrodes used in multilayer capacitors.

electrodes were deposited on to the tapes by screen printing, the electrode thickness being about 10 μm and the surface thickness 0.8 cm^2 (see Fig. 1).

Capacitors with five active layers were assembled by stacking. The stacked pads were then warm-pressed in a heated laminating die at 70 °C under 12.5 MPa pressure for 2 min to develop a good bond between the layers. Before sintering, the binder was burnt out by heating the samples at a rate of 0.5 °C min^{-1} up to a maximum of 500 °C, with a soak time of 1 h at this temperature. Then the samples were heated in an Al_2O_3 vessel with PbO volatilization control at a rate of 3 °C min^{-1} up to 1050 °C with a sintering soak time of 2 h. A silver termination paste was applied to the fired chips and then fixed on at 700 °C.

An X-ray diffractometer (Siemens 5000) with CuK_α radiation was used to identify the phases present in the sintered chips. A scanning electron microscope (Zeiss, DM-950) was used to study the microstructure of the sintered MLC and to measure the grain size.

Dielectric constant, capacitance and dielectric loss measurements were collected on a microcomputer using an impedance analyser (HP 4192 LF). Measurements were taken at 1, 10, and 100 kHz in the temperature range of $-50 - 150$ °C.

3. Results and discussion

Many physical anomalies can be present in a ceramic capacitor which can be produced during the different processing steps before sintering. If this is so then any crack, delamination or voids in the green ceramic capacitor will be strongly reproduced in the sintered one. Even when the ceramic capacitor requires a sintering temperature above 1000 °C, the different thermal expansion of both the electrode and the dielectric can initiate cracks if the heat treatment is not carefully carried out. All these lead to a low reliability of the multilayer ceramic capacitors. Therefore, careful control of the MLC fabrication process should be exerted in the two following ways: (a) a controlled elimination of the organic components of the tapes during the drying step, and (b) assuming good adhesion of the dielectric tape layers to dried electrode, careful control of both the burn-out and the co-firing steps must be made.

Fig. 2a shows the fracture surface of a green PMN–PZT multilayer capacitor, and Fig. 2b shows a delamination of unfired PMN–PZT multilayer capacitor as a consequence of a poor adhesion between the dielectric layer and the screen-printed electrode. Fig. 2c shows the fracture surface of a fired MLC in which the unfired delaminations produced fired delaminations.

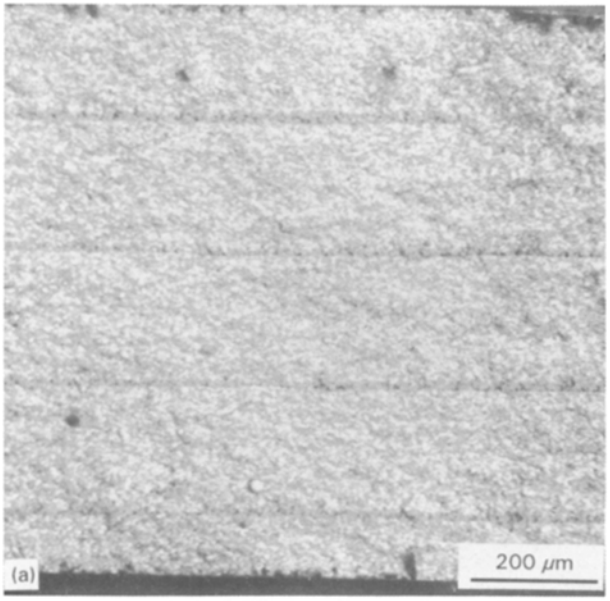
Given that some organic resins and solvents are added to the electrode paste in order to promote adhesion of the dielectric layer-printed electrode, the different exothermic reactions which will take place during the burn-out step, if not controlled, can contribute to the appearance of delaminations or other microstructure heterogeneities. Thus Fig. 3a shows some surface defects in a fired PMN–PZT multilayer capacitor, as a consequence of a poorly controlled resin decomposition reaction, and Fig. 3b and c show the heterogeneous evolution of the microstructure caused by the above-mentioned surface defects.

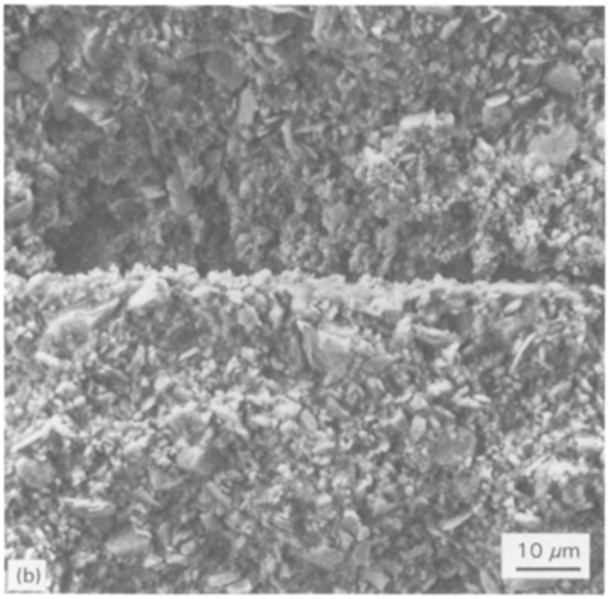
On the other hand, the different thermal expansions during the sintering step of both the dielectric layer and the electrode, also lead to delaminations. Fig. 4a shows a polished cross-section of a fired PMN–PZT multilayer capacitor observed by SEM. The density of the sintered MLC was always higher than 95% of the theoretical density and, as can be seen, with a uniformly distributed porosity. In spite of using high silver electrode alloys, some delamination phenomena were produced during the MLC sintering and, as can be observed in Fig. 4b, a separation of Ag/Pd electrode and PMN–PZT dielectric was present in some parts of the chip; this can be a serious quality problem for the performance of the MLC. An electrode composition with a thermal expansion coefficient lower than or near to that of the ceramic dielectric will lead to better behaviour.

Fig. 5 shows the X-ray diffraction pattern of the surface of sintered MLC in which neither PbO nor pyrochlore phase diffraction lines were detected. All the peaks correspond to the PMN–PZT solid solution perovskite phase.

Although the presence of high silver concentration in the Ag/Pd electrode limits palladium oxidation [9], a high diffusion of the oxidized silver to Ag_2O into the dielectric was clearly detected. Fig 6a shows a scanning electron micrograph in the vicinity of the electrode zone of the MLC, and a silver map is shown in Fig. 6b. A silver gradient towards the dielectric was revealed.

Although the microstructure, as shown in Fig. 7a, was quite uniform with an average grain size of 4 μm, the fracture is a mixture of the two intergranular and transgranular modes, indicating an inhomogeneous PbO distribution into the PMN–PZT grains. In spite of this, no pyrochlore phase grains either in the surface or in the interior of the dielectric, were observed,





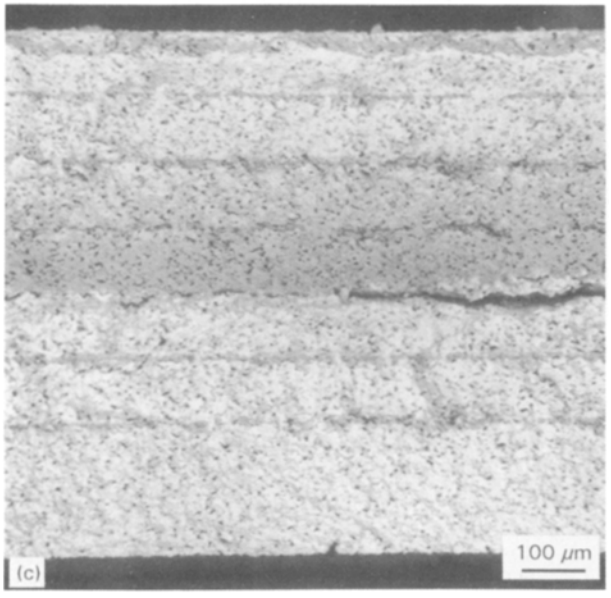
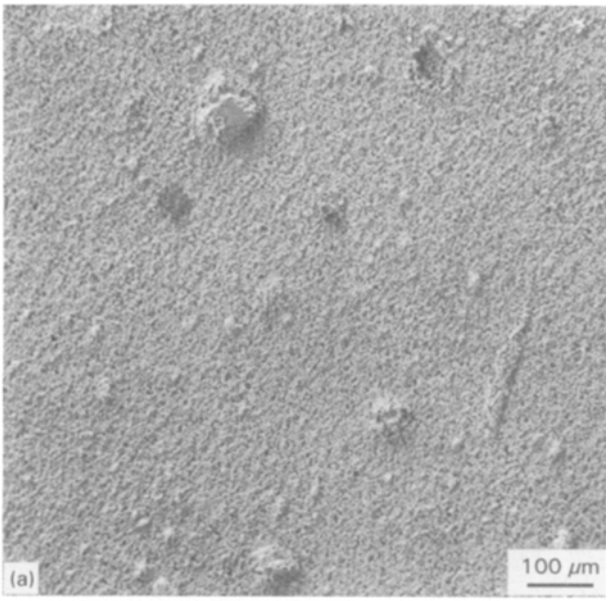
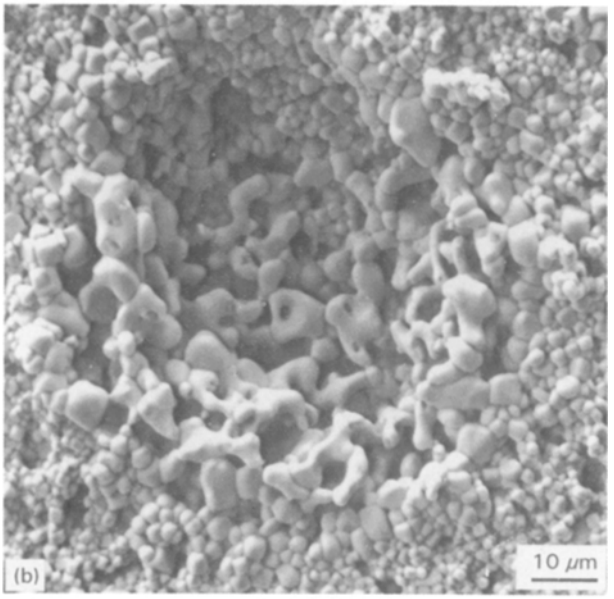


Figure 2 Micrographs of PMN–PZT capacitors: (a) green multilayer capacitor free of lamination; (b) green-state delamination; and (c) fired multilayer capacitor with delaminations.





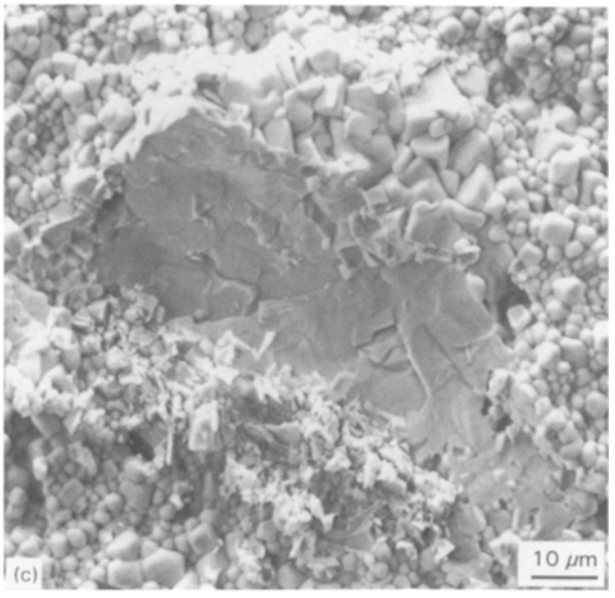


Figure 3 Micrographs of fired PMN–PZT multilayer capacitor showing (a) surface defects, and (b, c) microstructure heterogeneities.

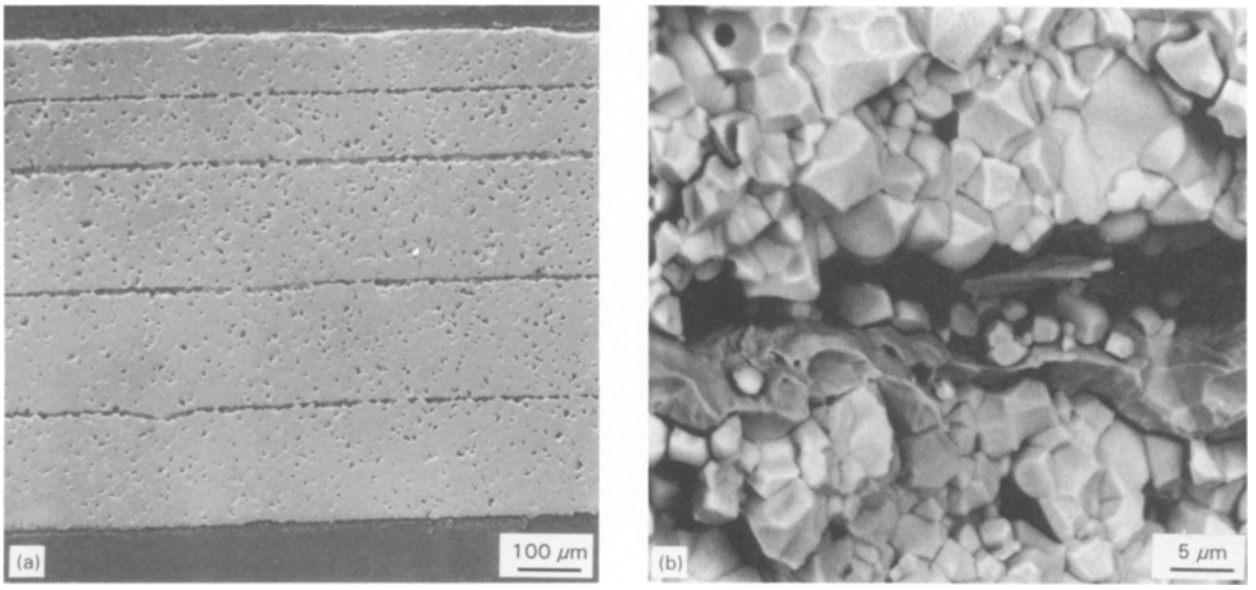


Figure 4 Polished cross-sections of a PMN–PZT fired MLC (a) without delaminations, and (b) shrinkage mismatch delaminations.

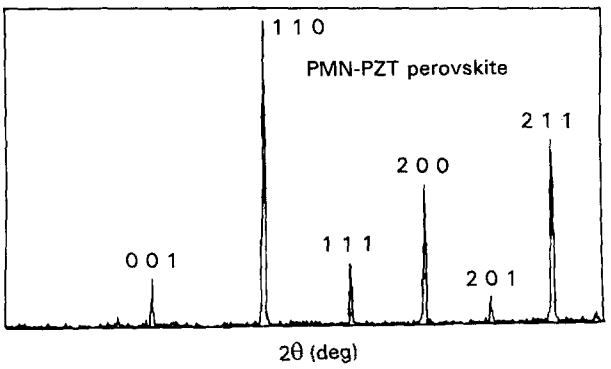


Figure 5 XRD pattern of PMN–PZT fired multilayer capacitor surface.

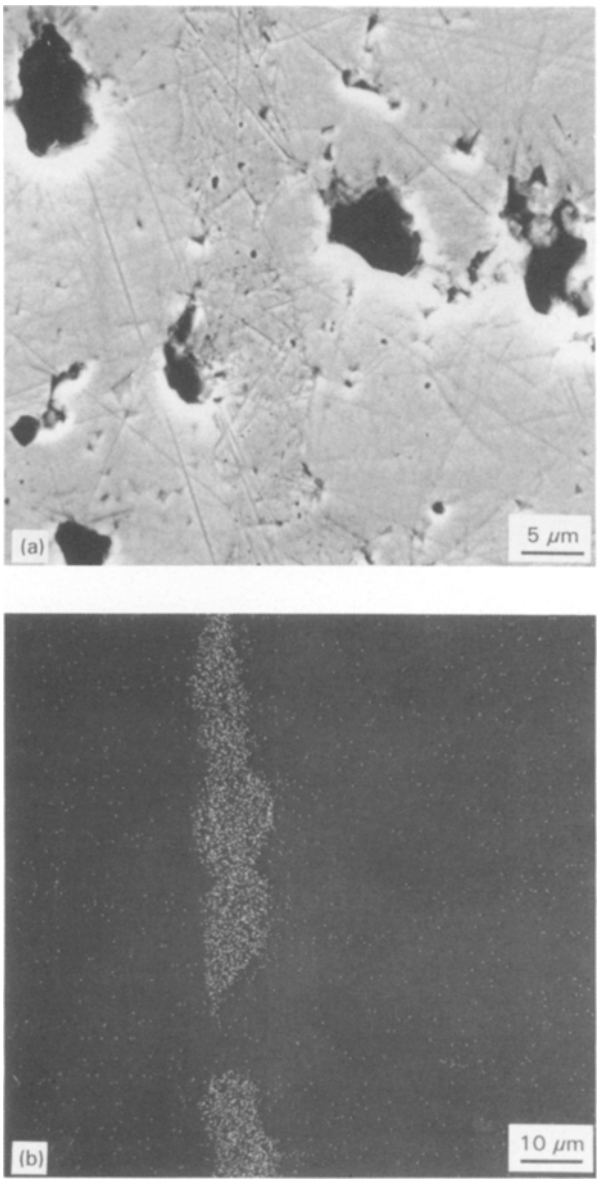


Figure 6 Polished cross-section of the electrode–dielectric in (a) a fired MLC, and (b) the silver mapping.

which indicated a good control of the PbO volatilization. This result is in contradiction to that reported by Landin and Schulze [10] who found the formation of a large amount of pyrochlore phase at the surface of rapidly sintered PMZN multilayer ceramic capacitors. The lack of PbO volatilization control could be the cause of the rapid formation of the pyrochlore phase.

It must be mentioned that although the microstructure of the dielectric layers was quite uniform, in the vicinity of the electrodes, a relatively exaggerated grain growth took place, see Fig. 7b. If it is taken into account that the silver oxide is stable from a temperature as low as 300 °C [11], the Ag_2O formed could be introduced into the perovskite structure strengthening its skeleton and thus inhibiting pyrochlore phase formation. At the same time, normal grain growth of the PMN–PZT ceramic could be affected by the small fluctuation of the Ag/Pd ratio produced in the electrode–dielectric contact region. If this is so, then our results could confirm those reported by Chu and Hodgkins [12] who found that the diffusion of silver into the ceramic could affect grain growth. Similar results were found by Maher [13], Ikusima and Hayakawa [14], and Wersing *et al.* [15] for $BaTiO_3$,

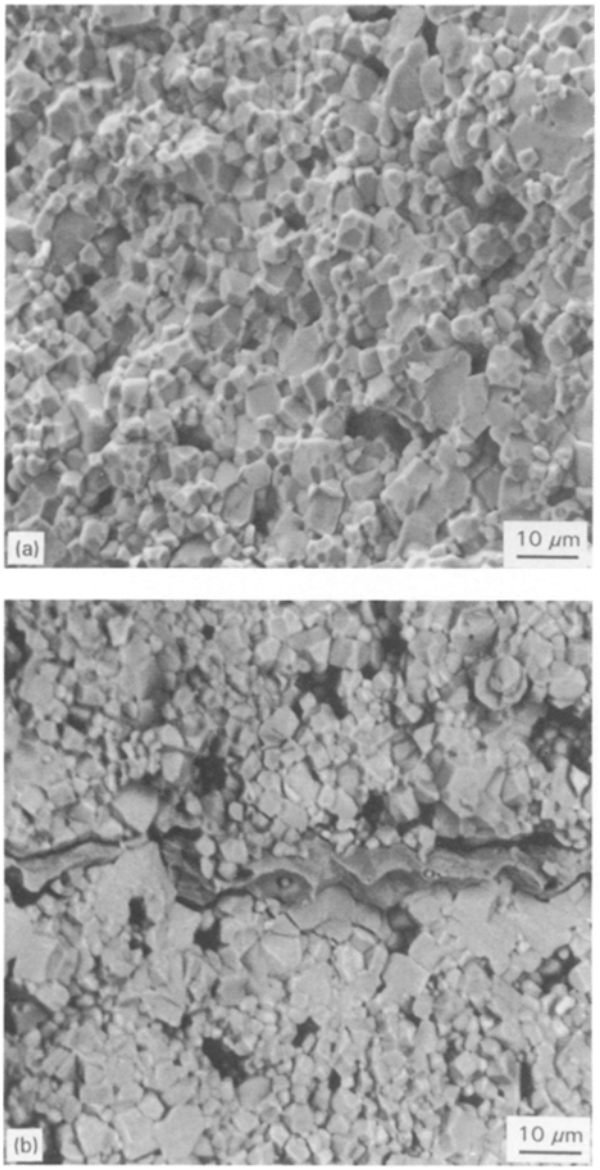


Figure 7 Microstructure development in (a) a fired PMN–PZT multilayer capacitor, and (b) abnormal grain growth in the vicinity of the electrode.

PLZT and PZT ceramics, respectively, when co-fired with silver-containing electrodes. In the different cases, both the microstructure and the electrical behaviour were influenced. Furthermore, as a consequence of the small variation of the Ag/Pd ratio, the activity of palladium in Ag/Pd alloys can be modified, allowing the formation of lower melting temperature Ag/Pd (Pb) alloys and, as a final result, the presence of delamination defects in the sintered PMN–PZT multilayer capacitor ceramics.

As shown in Fig. 8a the temperature dependence of the dielectric constant at various frequencies was according to the typical behaviour of the ferroelectric relaxors, and the largest maximum effective permitivity (~200 000) was centred very close to 25 °C and for a frequency of 1 kHz. This maximum then decreased as the frequency increased. Given that the dielectric constant is proportional to the capacitance, according to the equation $C/V = \varepsilon_0 K/t^2$ (where C is capacitance, V is volume, ε_0 is the absolute dielectric constant of a vacuum, K is the relative dielectric constant, and t is

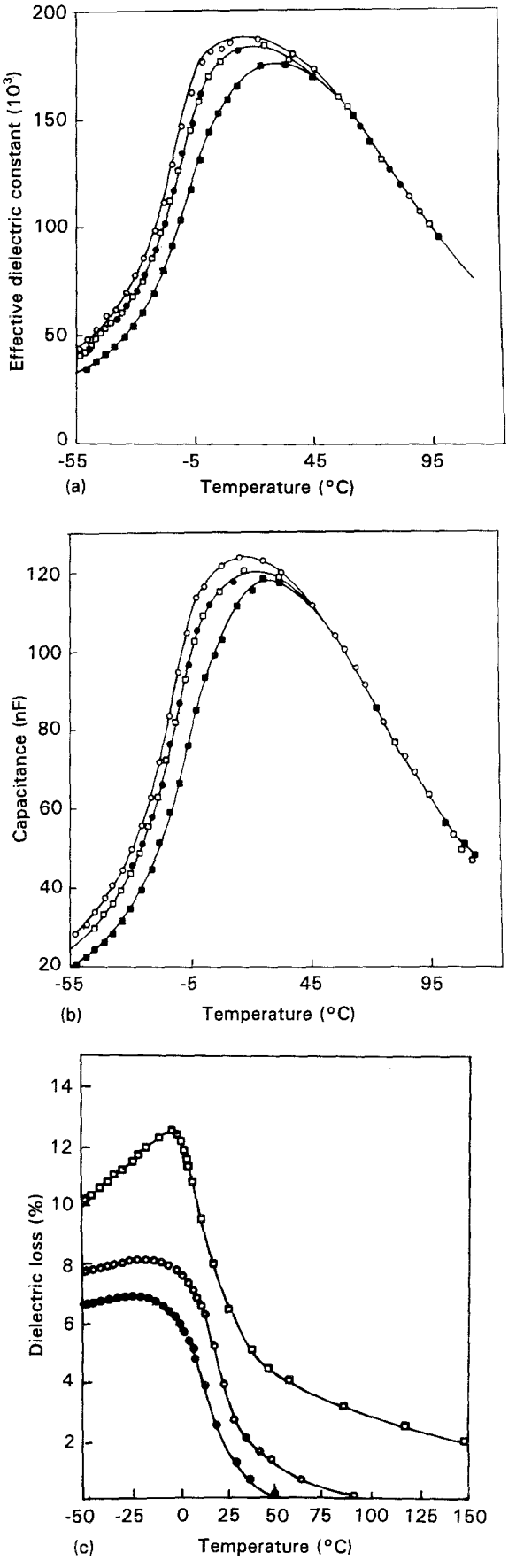


Figure 8 Temperature dependency of (a) the dielectric constant, (b) capacitance, and (c) dielectric loss, for a PMN–PZT multilayer capacitor sintered at 1050 °C for 2 h. (a, b) (○) 0.1 kHz, (●) 1 kHz, (□) 10 kHz, (■) 100 kHz. (c) (●) 1 kHz, (○) 10 kHz, (□) 100 kHz.

the thickness of the dielectric layer), the trend of the variation of capacitance with temperature was similar to that of the dielectric constant, showing a maximum in capacitance of 120 nF at a temperature of 24 °C, see Fig. 8b.

Fig. 8c shows typical plots of dielectric losses as a function of the temperature and, as expected, a clear dispersion of the dielectric losses with the frequency was present, and at a temperature range displaced with respect to that of the dielectric constant maxima. In both cases, in comparison to that of pure PMN [16], the frequency dispersion of the dielectric constant and of the dielectric losses were decreased by the presence of 10 mol% $PbTiO_3$–$PbZrO_3$ in the PMN–PZT solid solution.

4. Conclusion

Multilayer ceramic capacitors (MLCs) were made from $Pb(Mg_{1/3}Nb_{2/3})O_3$ powder doped with 10 mol% $PbTiO_3$–$PbZrO_3$, and a 70% Ag/30% Pd alloy was used as internal electrodes. Co-firing of five active layer chips was performed at 1050 °C for 2 h in a PbO-controlled atmosphere, and under such sintering conditions no detectable pyrochlore phase was present. As a consequence of the different sintering shrinkage characteristics of both the electrode and the dielectric, some delaminations were present in the sintered MLCs.

The microstructural development on sintered ($\geq$95% theoretical density) MLCs has been studied using SEM and EDX, and a quite uniform microstructure with grain size $<4\,\mu m$ was found. Some EDX studies indicated that an interaction between electrode and dielectric took place at the sintering temperature, and the Ag^+ ions diffused towards the interior of the dielectric. The Ag^+ diffusion influenced the normal grain growth process, giving rise to the formation of larger grains in the bulk microstructure of the fabricated MLCs.

The dielectric properties for five active layers MLC showed a good capacitance behaviour, and an effective dielectric constant maximum in excess of 180 000 was found near room temperature.

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