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Ceramic–electrode interaction in PZT and PNN–PZT multilayer piezoelectric ceramics with AG/PD 70/30 inner electrode

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$Pb(Zr_{0.53}Ti_{0.47})O_3$(PZT) and $PbNi_{1/3}Nb_{2/3}O_3$-PZT (PNN–PZT) multilayers with Ag/Pd 70/30 inner electrodes have been studied from the point of view of the ceramic–electrode interaction. PZT multilayers have shown silver free ceramic layers, and no lead has been detected in the electrode after sintering. Silver transport through the ceramic is avoided because of low open porosity–close porosity transition temperature. This transition seems to occur prior to the strong increase of the silver vapour pressure.

For PNN–PZT multilayers, similar behaviour to that commonly reported in the literature for PZT is observed. A constant amount of silver, independent of the distance from the electrode, is detected in the ceramic layer. Lead is also detected in the electrode. On the other hand, no interaction between ceramic and electrode has been observed for the other cations.

1. Introduction

Cofiring technique for the fabrication of multilayer piezoelectric ceramic (MLP) is the most promising for mass production and cost reduction. One of the main problems concerning MLP manufacturing is the choice of the inner electrode composition. Interaction between ceramic and electrode may change the sintering behaviour and final properties of the material; therefore, the reliability of the component also depends on this interaction [1]. Recently, many efforts have been made to determine the role of the inner electrode in the microstructural development of ceramic in multilayer structures [2–4]. For $Pb(Zr_{0.53}Ti_{0.47})O_3$(PZT) MLP's, platinum is an adequate electrode due to its inertness against reactions with PZT which allows nearly unchanged sintering conditions and a free ceramic composition. However platinum is very expensive, so, from a commercial point of view is necessary to replace it by cheaper electrodes. Ag/Pd 70/30 alloy is widely used to cofire multilayer ceramic capacitors and shows adequate characteristics to be utilized for MLP fabrication [2].

Interaction between Ag/Pd electrodes and PZT ceramic is reported in the literature. A considerable amount of the Ag originally present in the electrodes is transported into PZT matrix [2, 5]. Reported data show that the amount of silver detected in the ceramic is independent of the distance from the electrode; therefore, a fast silver transport mechanism must be involved. The strong increase of the silver vapour pressure above 1050 °C seems to favour silver transport through the open porosity as long as the PZT is not fully densified [5]. Because of silver loss, the electrode became palladium rich and the melting point of the electrode alloy increases [3, 4]. When increasing the temperature, Ag is incorporated into the lattice of the growing PZT grains [5]. On the other hand, vaporization of PbO through the open porosity leads to the formation of a thin Pd–Pb–O [4, 5] phase at the interface of PZT and Ag/Pd. Moreover, Pd(Pb) alloy or intermetallic $PbPd_3$ could be formed, changing the electrode composition to Ag/Pd(Pb). Such reactions may be responsible for the good bonding and mechanical strength of the interface PZT electrode, but also modify the sintering behaviour and final piezoelectric properties.

Some properties of PNN–PZT ceramics may be better than those of the conventional PZT binary system ceramics. In previous works, doped PNN–PZT materials are reported, maintaining high piezoelectric properties at low sintering temperatures [6]. In view of this, PNN–PZT ceramics may be promising candidates for MLP devices. However, interaction between Ag/Pd inner electrode and ceramic PNN–PZT in multilayer structures are not reported in the reviewed literature; hence, no information about the mechanisms involved is available up to date.

The main goal of this work has been to elucidate what is the behaviour of a Ag/Pd electrode/ceramic interphase in MLP devices containing PNN and

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the influence of metallic activity on the ceramic microstructure and piezoelectric characteristics, taking into account the presence of NiO in the ceramic composition.

2. Experimental procedure

Synthesis and characterization of the PZT (53/47) powder have been previously reported [7]. 0.6PNN–0.4PZT powder was supplied by Quartz & Silice, and it has been obtained by conventional solid state route. Fig. 1 shows a scanning electron microscope (SEM) micrograph of the powder and its main characteristics are summarized as follows

Specific surface area, $S_A = 0.83\ \mathrm{m^2\,g^{-1}}$

Particle size $\sim 4\ \mu\mathrm{m}$,

Second phases = 10% $Pb_3Nb_4O_{13}$ (by X-ray diffraction (XRD) analysis)

PZT and 0.6PNN–0.4PZT ceramic sheets were obtained by tape casting. Slip formulation was a classical one [8] where ester phosphate was added as a dispersant agent. Ag70/Pd30 paste was screen printed as the inner electrode. The stacks were pressed and fired according to the following schedule:

- burn-out: 700 °C 1 h and heating rate of 0.5 $^\circ\mathrm{C\ min^{-1}}$
- sintering: temperatures ranging from 1050 to 1150 °C for 2 h soaking time and heating and cooling rates of 3 $^\circ\mathrm{C\ min^{-1}}$.

Sintering treatment was performed without buffer for both cases (PZT and PNN–PZT). After sintering, ceramic multilayer devices with 10 layers about 60 μm thickness each and five inner electrodes about 5–10 μm thickness are obtained. Ceramic–electrode interaction and microstructural evolution have been studied for multilayers sintered at different temperatures. For PZT multilayers, samples sintered at 1050, 1075, 1100, 1125 and 1150 °C were polished and chemically etched to follow the microstructural evolution by means of reflected light optical microscopy (RLOM) and SEM. Cation diffusion, specially silver and lead diffusion, have been measured by electron probe microanalysis (energy dispersive spectroscopy EDS) and (wavelength dispersive spectroscopyWDS) over polished surfaces of the samples sintered at 1050, 1100 and 1150 °C. The sample sintered at 1125 °C was prepared (cut and ion milled) for transmission electron microscopy (TEM) analysis. Porosimetry measurements, by means of a mercury porosimeter, were performed on tape-cast samples without electrode and heat treated from 1050 to 1200 °C.

PNN–PZT multilayers were sintered at 1100, 1125 and 1150 °C with the same firing schedule that was used for PZT multilayers. After polishing and chemical etching, microstructure was studied by RLOM and SEM. Electron probe microanalysis (EPMA) was performed for the samples sintered at 1100 and 1150 °C. The sample sintered at 1125 °C was prepared for TEM analysis.

3. Results and discussion

3.1. PZT Multilayers

PZT multilayers show a homogeneous, fine grained microstructure. Grain size of about 1–2 μm and low porosity is observed. High density ceramic is obtained even for sintering temperature as low as 1050 °C (Fig. 2a). Sintering occurs with strong grain growth inhibition (Fig. 2b). Porosity seems to change for the sample sintered at 1150 °C; however, no significant

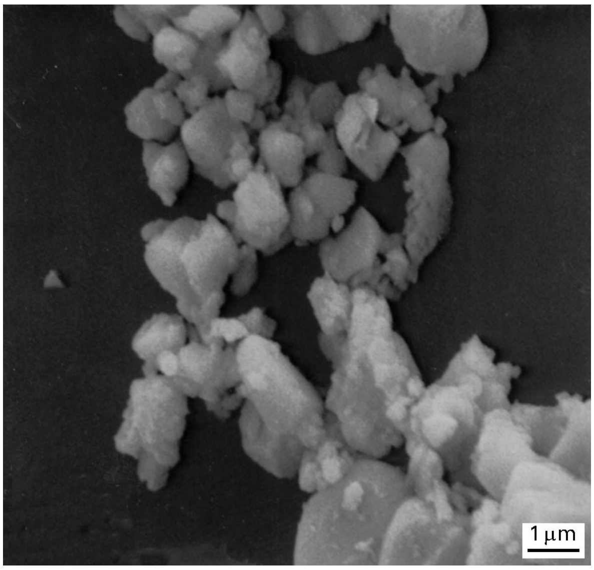

Figure 1 SEM micrograph of PNN–PZT ceramic powder.

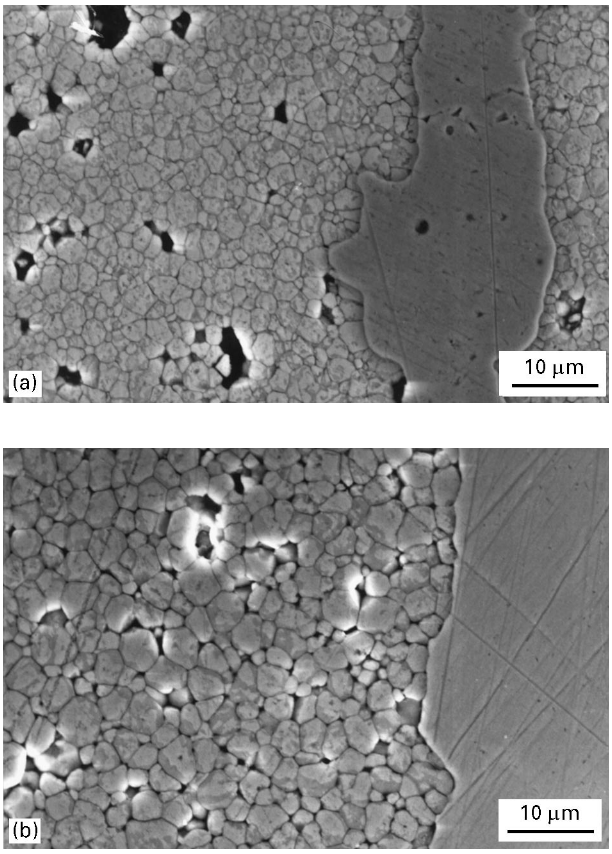

Figure 2 SEM micrographs on polished surface of PZT multilayer material sintered at (a) 1050 °C; (b) 1150 °C, and 2 h soaking time.

changes in the microstructure are detected when increasing sintering temperature. Ceramic electrode contact is good in all cases.

Ag content in the ceramic layer and PbO content in the electrode were checked by EPMA. Line profiles and mapping of all the cations were performed. No Ag was detected in the ceramic, and the same behaviour was observed for Pb in the electrode (Fig. 3). The performed WDS analysis allowed to detect 0.01% (in this case) of Ag or Pb in the ceramic or electrode, respectively; however, the number of counts are typically background ones.

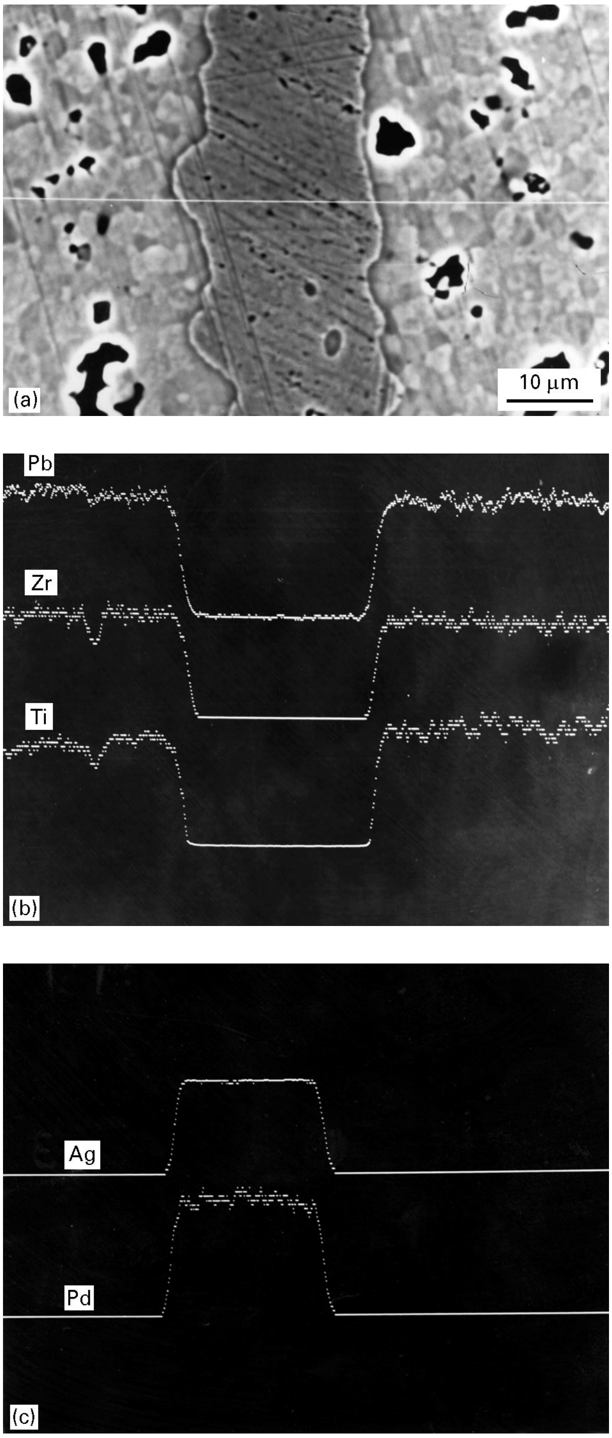

Figure 3 (a) Bright field image and (b, c) line profiles obtained by SEM on the surface of PZT multilayer sample fired at 1050 °C. Ag and Pd are detected only in the electrode; Pb, Zr, Ti are detected in the ceramic.

TEM analysis showed the same result concerning to Ag and Pb diffusion. No Pd–Pb–O second phase was detected at the interface between ceramic and electrode. On the other hand, PbO and residual phosphorus from ester phosphate were found in some triple points (Fig. 4).

Porosity curves (Fig. 5) show that the transition from open porosity to closed one occurs at low temperatures between 1050 and 1100 °C. Above this range of temperatures a strong increase of Ag vapour pressure takes place [2]. It seems that the early transition

Figure 4 TEM micrograph obtained on a PZT multilayer sample fired at 1125 °C, showing a triple point filled with a liquid phase containing phosphor.

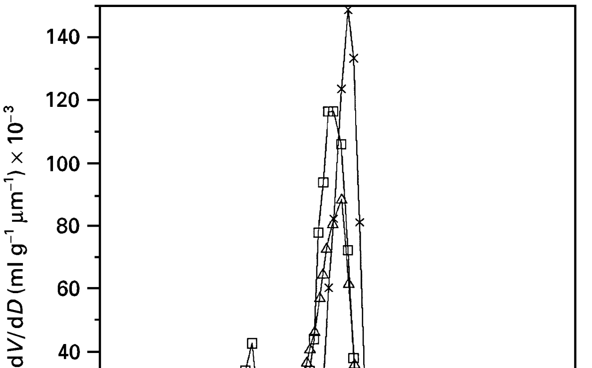

Figure 5 Porosimetry curves of green and different temperature-fired PZT samples. (×) 950 °C; (△) 1000 °C; (□) 1025 °C; (∗) 1050 °C.

from open porosity to closed porosity, avoids Ag transport and PbO electrode interaction. Ester phosphate may play an important role in this case. For tape-cast Al_2O_3 [9] and $BaTiO_3$ [10] residual phosphorus adsorbed onto the particles' surfaces causes strong grain growth inhibition and favours porosity coalescence and elimination at first stage sintering. This could be the reason for the small grain size detected and the absence of Ag in the ceramic.

3.2. PNN–PZT multilayers

PNN–PZT multilayers show heterogeneous microstructure with different grain sizes. Porosity decreases when sintering temperature increases. The density of these multilayers sintered at 1125 °C was relatively low (Fig. 6) but higher than that of the isopressed pellets sintered at the same temperatures. Therefore, multilayer structures reach higher density for lower temperatures. The microstructure of sintered samples revealed a three-phase material: expected PNN–PZT solid solution, ZrO_2 (Fig. 7a) and NiO (Fig. 7b). The morphology and distribution of these phases suggest their presence in the original powder as unreacted products. On the other hand, pyrochlore phase $Pb_3Nb_4O_{13}$ was not detected.

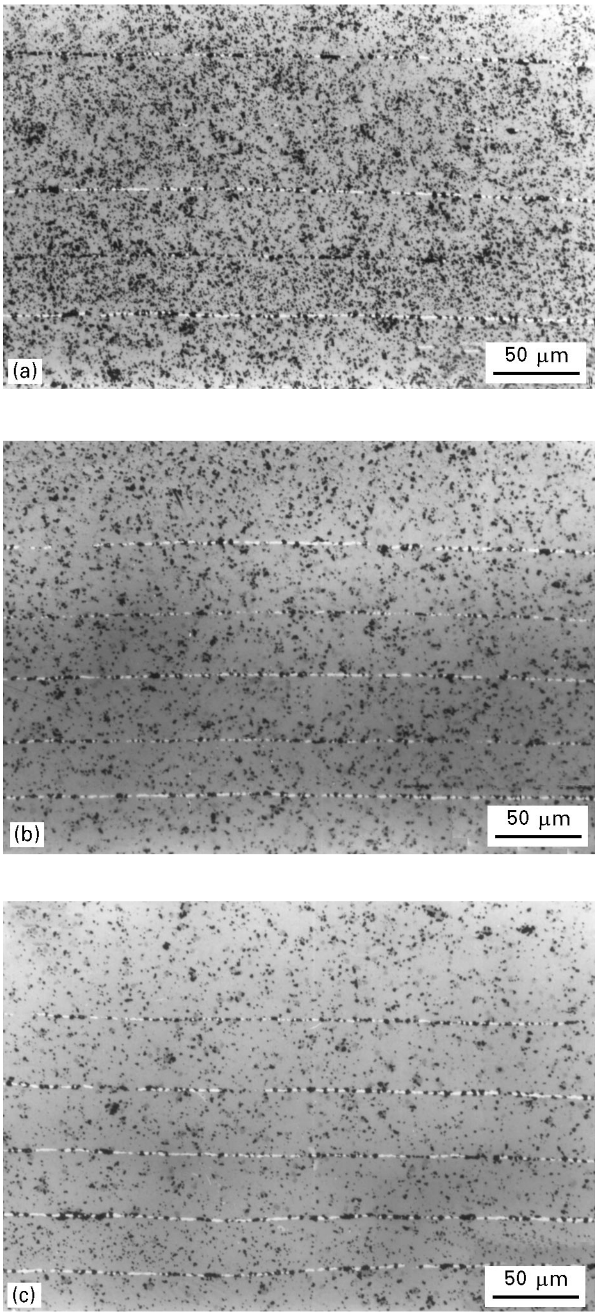

Figure 6 RLOM micrographs of PNN–PZT multilayer samples fired at (a) 1100 °C; (b) 1125 °C; (c) 1150 °C.

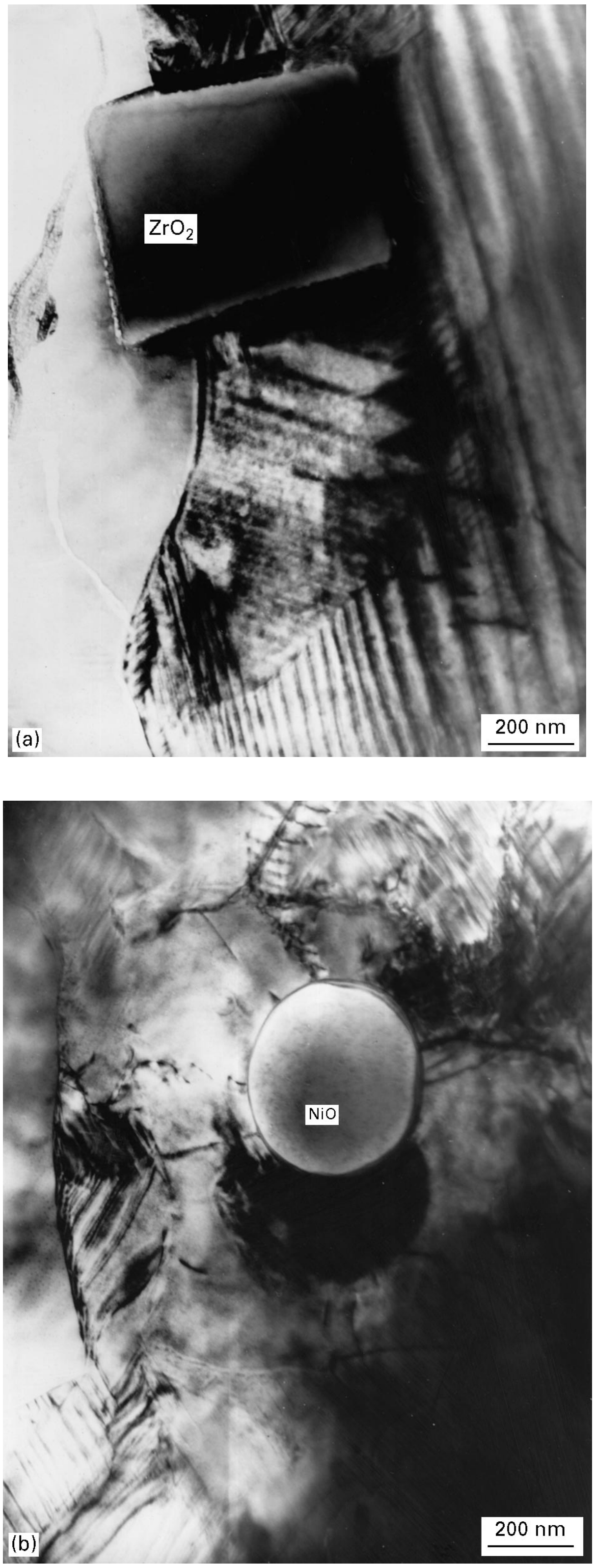

Figure 7 TEM micrograph of PNN–PZT sample sintered at 1125 °C, showing inclusions of (a) ZrO_2 and (b) NiO.

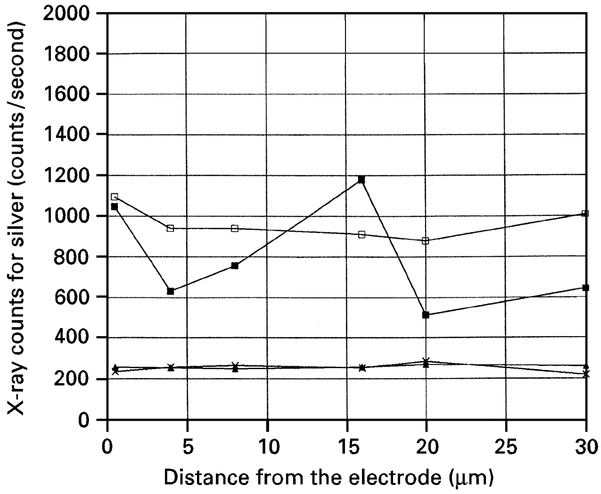

Figure 8 WDX semiquantitative analysis of Ag content in a PNN–PZT ceramic layer for samples sintered at 1100 °C (B_1); and 1150 °C (B_3). (■) Ag peak counts: B1; (□) Ag peak counts: B3; (×) background: B1; (▲) background: B3.

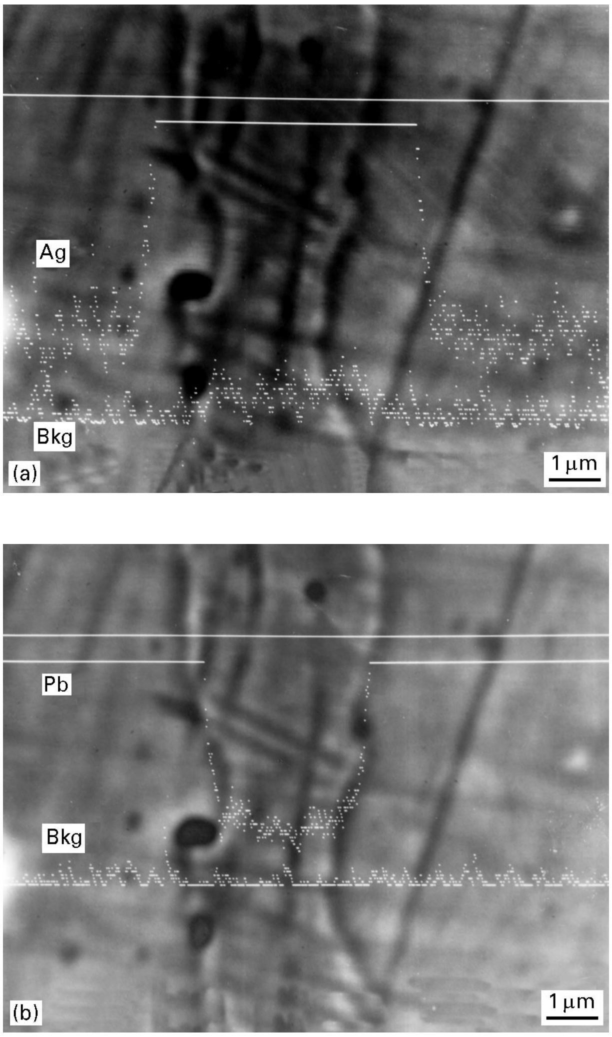

Figure 9 Line profiles of (a) Ag, (b) Pb and background counts on a PNN–PZT sample fired at 1150 °C.

The ceramic layers showed a constant of Ag detected by WDX (Fig. 8), and the same result is obtained for Pb in the electrode. The exact amount of Ag in the ceramic and Pb in the electrode has not been determined because of the difficulty in measuring such small amounts. Ag concentration is constant and independent of the distance from the electrode, as reported in the literature for PZT multilayers (Fig. 9). Line profiles and mapping of other cations show no interaction between ceramic and electrode. This behaviour is the same for the samples sintered at 1100 and 1150 °C.

TEM analysis of the sample sintered at 1125 °C (Fig. 10) confirmed SEM results for the other samples. No Pb–Pd–O phase has been detected; therefore, if it exists must be very thin.

Interaction between electrode and PNN–PZT can be explained in a similar way to that reported in the literature for PZT. For the PNN–PZT material studied, transition to closed porosity takes place after the strong increase of Ag vapour pressure. Although residual phosphorus seems to cause the decrease of sintering temperature for multilayer structure, heterogeneity of the starting powder drives to very high sintering temperatures. Therefore Ag transport and PbO–electrode interaction takes place, being favoured for the existence of porosity channels in the ceramic at temperatures higher than that corresponding to the strong increase of Ag vapour pressure.

4. Conclusions

PZT multilayers with Ag free ceramic layers have been obtained and no interaction between Pb and electrode is detected. This result can be explained on the basis of the low temperature of open–closed porosity transition, which avoids the Ag transport through the hollow spaces of the ceramic. Such a behaviour can be

Figure 10 TEM micrograph of a PNN–PZT sample fired at 1125 °C showing a three-grain junction free of liquid phase.

related to the presence of residual phosphorus incorporated with the dispersant agent (ester phosphate) used for the slip preparation, which forms a low temperature liquid phase that promotes a fast densification process, or to the small particle size of the powders which leads to a higher densification kinetic.

Interaction between PNN–PZT and Ag/Pd electrode occurs like that reported in the literature for PZT. No significant effects have been detected for Ni and Nb cations. Ceramic layers show a constant amount of Ag independent of the distance from the electrode. Pb is also detected in the electrode. In this case phosphorus cation presence decreases the sintering temperature but it remains even too high because of the powder heterogeneity and the presence of unreacted phases. Therefore open–closed porosity transition takes place after the strong increase of Ag vapour pressure, so that Ag may diffuse through the porosity channels of the ceramic layer.

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