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Microstructural and electrical characterisation of PZT thick films on LTCC substrates

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Abstract

Piezoelectric thick films based on $Pb(Zr,Ti)O_3$ (PZT) were prepared on two types of LTCC tapes (Du Pont 951 and Electro Science Labs. 41020) and on relatively inert alumina substrates. The results obtained with the alumina were used as a reference. The microstructures of the cross-sections of the resistors were investigated using scanning electron microscopy (SEM) and energy-dispersive X-ray (EDS) analysis. The dielectric permittivities, dielectric losses, remanent polarisation, coercive field and piezoelectric constant d_{33} were measured. The dielectric and piezoelectric characteristics of the PZT fired on the LTCC substrates deteriorated in comparison to the samples on alumina, due to interactions between the LTCC substrate and the PZT layer. Lower dielectric constants, remanent polarisations and piezoelectric constants indicate the formation of phases with a low permittivity. This was attributed to the diffusion of SiO_2 from the LTCC into the active PZT layer and to the diffusion of PbO from the PZT layer into the LTCC substrate. The diffusion was confirmed by the SEM and EDS analysis.

Keywords: Dielectric properties; Piezoelectric properties; PZT; Sensors; LTCC

1. Introduction

Piezoelectric ceramics are used in a wide range of sensors, actuators and transducers that are important in diverse fields, such as industrial process control, environmental monitoring, communications, information systems, and medical instrumentation.

For some microelectronic and micro-electro-mechanical systems (MEMS) applications the active piezoelectric layer should be a few 10 s of μm thick. Thick-film technology, i.e., the deposition of a thick-film paste by screen printing onto substrates is a relatively simple and convenient method for producing layers with thicknesses of up to 100 μm. The characteristics of thick-film piezo- and ferroelectrics are similar to those of the bulk materials. The compositions of piezoelectric thick-films are mainly based on $Pb(Zr_{1-x}Ti_x)O_3$, referred to as PZT [1–4]. The solid solutions have, for compositions near the morphotrophic phase boundary of $Pb_{0.53}Ti_{0.47}O_3$ (PZT 53/47), a room-temperature dielectric constant of a little less than 1000 and a piezoelectric coefficient of around 200 pC/N. The characteristics of screen-printed PZT thick films on alumina substrates were first described, to the best of the authors' knowledge, in 1987 by Boudry [5].

The processing temperatures required to obtain dense, bulk PZT ceramics are around 1200 °C. This is too high for thick-film technology, where the firing temperatures are between 800 °C and 900 °C. To be able to make use of these processing temperatures the basic PZT compositions need to be modified. The sintering temperatures can be lowered with the addition of low-melting-point oxides or compounds [5,6–9]. The substrates for thick PZT films, as reported in the open literature, are mainly alumina or silicon [3–6,10,11].

LTCC (low-temperature co-fired ceramic) materials, which are sintered at the low temperatures typically used for thick-film processing, i.e., around 850 °C, are based either on crystallisable glass or a mixture of glass and ceramics [12–14]. They have some advantages over alumina substrates: mainly a lower

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Young's modulus (alumina 215–414 GPa, LTCC 90–110 GPa), which is important for sensors and actuators. However, the glass phase in LTCC materials might interact with thick-film PZT layers fired on LTCC tapes, leading to changes in the electrical characteristics.

The aim of this work was to study the microstructural, electrical and piezoelectric characteristics of thick PZT films on two LTCC tapes, i.e., Du Pont (DP) 951 and Electro Science Labs. (ESL) 41020. The ESL 41020 is a lead-free material, while the DP 951 contains between 2 and 3 mol.% of PbO. PZT films were also made on relatively inert alumina substrates. The results obtained from the alumina-based experiments were used as a reference. The dielectric permittivities, ε', dielectric losses, $\tan\delta$, remanent polarisation, P_r, coercive fields, E_c, and piezoelectric constants, d_{33}, were measured.

2. Experimental

$PbZr_{0.53}Ti_{0.47}O_3$ (PZT 53/47) powder with an excess 6 mol.% of PbO was prepared by mixed-oxide synthesis at 900 °C for 1 h from high-purity PbO (litharge, 99.9% Fluka), ZrO_2 (99%, Tosoh), and TiO_2 (99%, Fluka). To this was added 2 wt.% of lead germanate, with the nominal composition $Pb_5Ge_3O_{11}$ (melting point 738 °C) as a sintering aid. A thick-film paste was prepared from the PZT (2% PGO) and an organic vehicle. The LTCC substrates were made by laminating three layers of LTCC tape at 70 °C and a pressure of 20 MPa. The laminated green tapes were fired for 1 h at 450 °C (organic binder burnout) and 15 min at 875 °C.

A thick-film gold conductor was printed on the substrates and fired at 850 °C. The PZT paste was printed twice and fired at 850 °C for 20 min, and then again printed twice and fired for the same time. Then the upper gold electrode was printed and fired at 850 °C. As a reference the same thick-film PZT structures were processed on relatively inert 96% alumina substrates.

For the microstructural investigation the samples were mounted in epoxy in a cross-sectional orientation and then cut and polished using standard metallographic techniques. A JEOL JSM 5800 scanning electron microscope (SEM) equipped with an energy-dispersive X-ray analyser (EDS) was used for the overall microstructural and compositional analysis. Prior to analysis in the SEM, the samples were coated with carbon to provide electrical conductivity and to avoid charging effects. Note that boron oxide, which is also present in the glass phase of LTCC substrates, cannot be detected in the EDS spectra because of the low relative boron weight fraction in the glass and the strong absorption of the boron Kα line during EDS analysis in the glass matrix.

For measurements of the piezoelectric coefficients one can use either the direct piezoelectric effect (applying a stress and measuring the induced charge) or use the inverse piezoelectric effect (applying a voltage and measuring the induced strain). In principle, both methods make it possible to measure the piezoelectric coefficient d_{33}. If we choose the direct effect, then d_{33} is defined as:

$$D_3 = d_{33}\sigma_3, \tag{1}$$

Table 1
Piezoelectric coefficients for the PZT composition [17]

d_{33} (pC/N)	d_{31} (pC/N)	s_{11}^E (pm^2/N)	s_{12}^E (pm^2/N)	s_{13}^E (pm^2/N)
223	−93.5	13.8	−4.07	−5.8

where D_3 is the component of the dielectric displacement vector (As/m^2) and σ_3 the component of the stress matrix (N/m^2). However, for a measurement of the piezoelectric properties of thin and thick films one has to keep in mind that the film is clamped to a substrate. Therefore, the ratio D_3/σ_3 does not represent the piezoelectric coefficient d_{33} of the free sample, but an effective coefficient [15,16]:

$$d_{33}^{\text{eff}} = d_{33} - 2d_{31}\frac{(\nu/Y) + s_{13}^{\text{E}}}{(s_{11}^{\text{E}} + s_{12}^{\text{E}})}, \tag{2}$$

where d_{33} and d_{31} are piezoelectric coefficients (pC/N or m/V) of the PZT material, the $s_{13}^{\text{E}}, s_{11}^{\text{E}}, s_{12}^{\text{E}}$ are elastic compliance coefficients at a constant electric field (m^2/N) for a PZT material, and ν and Y are the Poisson's ratio and Young's modulus of the substrate, respectively. The values for the coefficients in Table 1 were taken from [17].

The dielectric permittivity and dielectric losses were measured with an HP 4284 Precision LCR Meter at 1 kHz. The values of the remanent polarisation and the coercive field were determined from ferroelectric hysteresis curves measured with an Aixact TF Analyser 2000 at 50 Hz. The real and the imaginary parts of the complex dielectric constant were measured with an HP 4284 A Precision LCR Meter at 1 kHz. The samples were heated in an oil bath to 160 °C and poled with an electrical field of 10 kV/mm for 15 min, and cooled down to room temperature. The piezoelectric constant d_{33} was measured using the Berlincourt method at 100 Hz with the Take Control PM 10 piezometer. The Poisson's ratios and Young's moduli of the substrates required for a calculation of the effective d_{33} of the thick films (see Eq. (2)) were measured using a nano-indentation technique [18].

3. Results and discussion

The X-ray spectra of the Du Pont LTCC 951 [19,20] and the ESL 41020 tapes, unfired and fired at 875 °C, are shown in Fig. 1a and b, respectively. The unfired DP 951 tape is a mixture of alumina and glass, while the crystalline phases in the unfired ESL tape are alumina and gahnite (zinc aluminate $ZnAl_2O_4$). The peaks of alumina and the zinc aluminate are denoted by "A" and "Z", respectively. After firing, peaks of other phases that crystallised from the glass phase can be observed. For the DP 951 peaks of anorthite ($(Na,Ca)(Al,Si)_4O_8$) phase (denoted by an asterisk) appeared. For the ESL 41020 more phases can be observed after firing, i.e., celsian $BaAl_2Si_2O_8$ (denoted "B"), quartz (denoted "SiO_2") and larnite Ca_2SiO_4 (denoted "C"). Few small peaks denoted "?" could not be identified.

The microstructures of the DP 951 and ESL 41020 are shown in Fig. 2a and b, respectively. Both LTCC materials are a mixture of a darker alumina-rich phase and a lighter silica-rich glassy

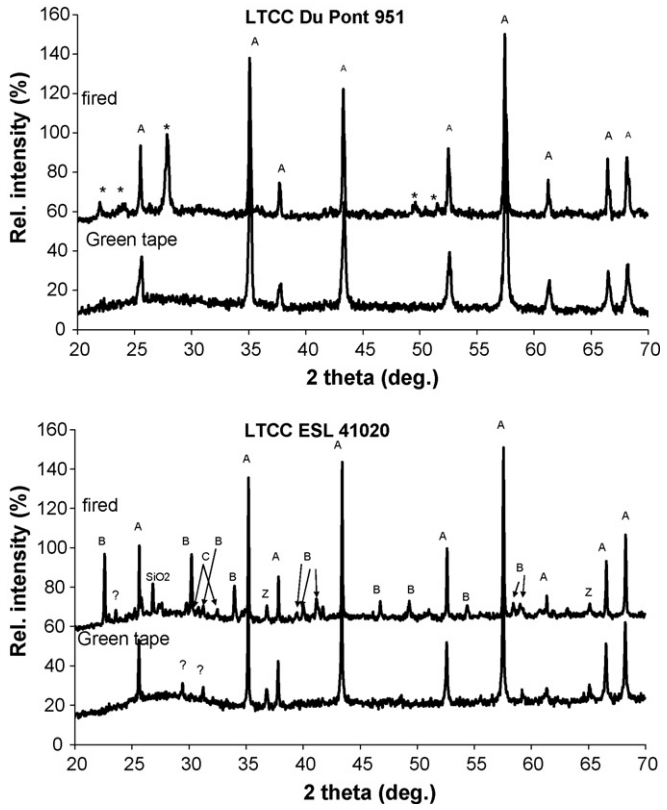

Fig. 1. (a) X-ray spectra of green and fired (875 °C) Du Pont LTCC 951 tapes [11]. The peaks of alumina and anorthite are denoted "A" and asterisk, respectively. (b) X-ray spectra of green and fired (875 °C) ESL LTCC 41020 tapes. The peaks of alumina are denoted "A", of celsian BaAl2Si2O8 "B", of quartz "SiO2", of gahnite ZnAl2O4 "Z" and of larnite Ca2SiO4 "C". Unidentified peaks are denoted by question mark.

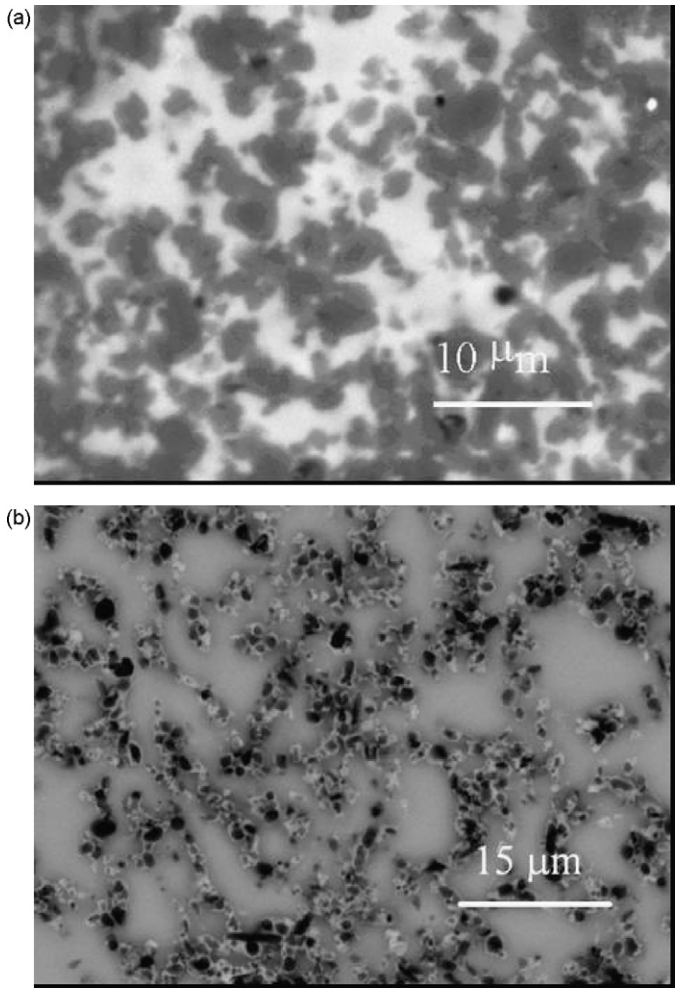

Fig. 2. (a) Microstructure of Du Pont 951 LTCC fired at 875 °C. (b) Microstructure of ESL 41020 LTCC fired at 875 °C.

phase. The analysis of the white particles in the ESL LTCC microstructure showed mainly Si, and this is presumably the silica phase (quartz) detected in the X-ray analysis.

The EDS analyses of the DP and ESL LTCC materials are shown in Table 2 and are graphically presented in Fig. 3. The concentrations of oxides are given in mol. percents. Both LTCC materials are "rich" in silica and alumina. Al_2O_3 is added as a ceramic filler, but it is also part of the glass, at least after firing. Both also contain a small concentration, between 0.1 and 0.2%, of cobalt oxide, which is added to give a blue colour. The DP 951 also contains some alkaline oxides (K_2O and Na_2O) and around 2 mol.% of PbO. The composition of the lead-free ESL 41020 is relatively rich in CaO (4 mol.% in DP 951 and 12 mol,% in ESL 41020). It also contains BaO, which is not present in the DP 951 material.

Table 2
The EDS analyses of the DP 951 and ESL 41020 LTCC materials in (mol.%)

	Du Pont 951	ESL 41020
$NaO_{0.5}$	2	
$AlO_{1.5}$	53	39
SiO_2	36	39
$KO_{0.5}$	1	
CaO	4	12
$CoO_{1.5}$	<0.2	<0.2
ZnO		2
BaO		8
PbO	2	

The microstructures of the PZT thick films fired on the LTCC substrates are shown in Fig. 4a and b for films on DP 951 LTCC and ESL 41020 LTCC, respectively. A lighter layer is formed at the interface between the gold electrode and the LTCC. The

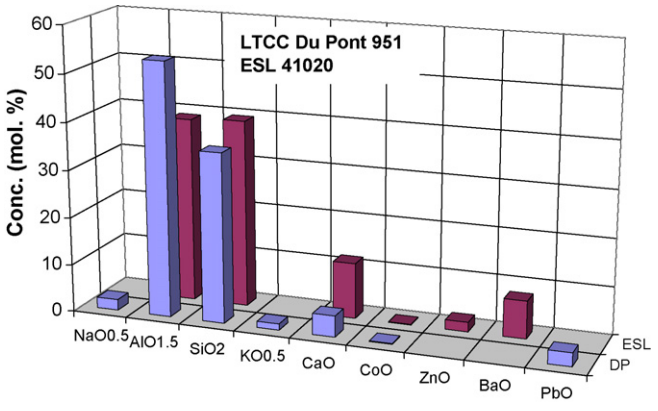

Fig. 3. EDS analysis of Du Pont 951 and ESL 41020 LTCC materials.

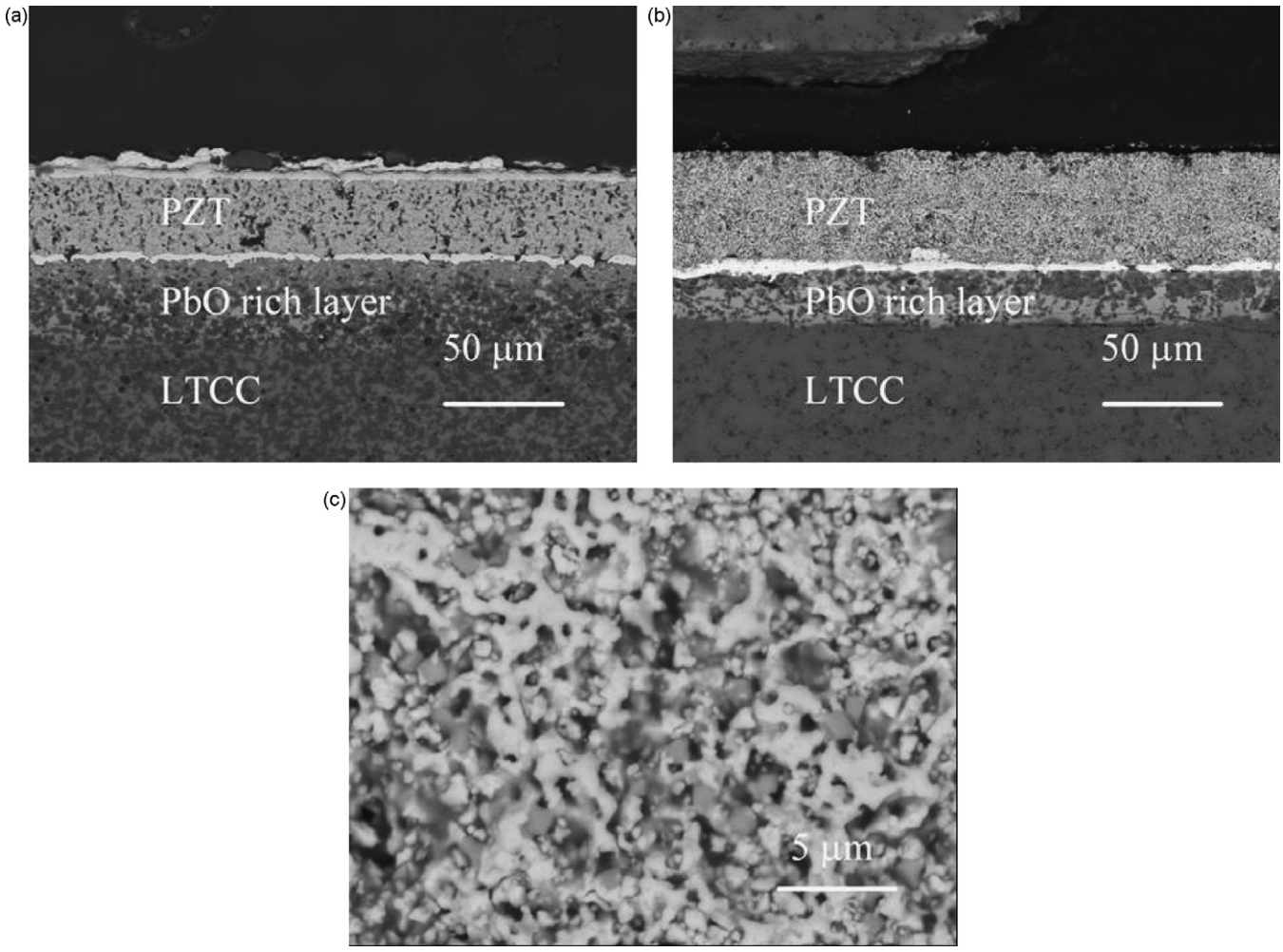

Fig. 4. (a) Microstructure of the cross-section of the DP 951 LTCC/gold/PZT structure, fired at 850 °C. Back-scattered electrons image. (b) Microstructure of the cross-section of the ESL 41020 LTCC/gold/PZT structure, fired at 850 °C. Back-scattered electrons image. (c) Microstructure of the PZT layer on ESL 41020 LTCC substrate. Back-scattered electrons image.

thickness of this layer is around 50 μm for the DP 951 and around 25 μm for the ESL 41020. The light layer is rich in PbO (around 30 wt.%). The diffusion of ZrO_2 and TiO_2 from the PZT into the LTCC was not detected. The microstructure of the PZT film is shown at a higher magnification in Fig. 4c. During firing the PZT solid solution decomposed into a two-phase mixture of darker and lighter grains.

The EDS analysis of the PZT films on LTCC substrates and on alumina substrates are presented in Table 3. The EDS micro-analysis of the PZT layers showed, in addition to Pb, Zr and Ti, a high concentration of Si (14 mol.% and 23 mol.% of SiO_2 for DP 951 and ESL 410202, respectively), Al (6 mol.% of $AlO_{1.5}$, only for DP 951) and also some Ca (around 2 mol.% of CaO).

Table 3
EDS analysis of cross-sectioned samples of PZT thick films on LTCC (DP 951 and ESL 41020) and Al_2O_3 substrates (mol.%)

	Du Pont	ESL	Al_2O_3
$AlO_{1.5}$	6		
SiO_2	14	22	
CaO	1	1	
TiO_2	21	19	27
ZrO_2	21	21	23
PbO	38	38	50

Table 4
EDS analysis of dark and light phases in PZT film fired on LTCC substrate (mol.%) (PZT and LTCC analyze SEM Darko-Marina-XLS)

	Dark phase	Light phase
SiO_2	12	16
CaO	8	<1
TiO_2	10	20
ZrO_2	55	18
PbO	15	45

Table 5
Poisson's ratios and Young's moduli of the materials measured using a nano-indentation technique

	Al_2O_3	DP 951	ESL 41020
ν	0.22	0.17	0.17
Y (GPa)	340	65	110

Table 6
Dielectric permittivity, ε', the dielectric loss, tan δ, remanent polarisation, P_r, coercive field, E_c, and piezoelectric constant, d_{33}, of the PZT thick films fired the on the alumina and LTCC substrates

Sample	ε' (1 kHz)	tan δ (1 kHz)	P_r (μmC/cm^2)	E_c (kV/cm)	d_{33} (meas.) (pC/N)	d_{33} (calc.) (pC/N)
ESL LTCC	105	0.7×10^{-2}	3.0	81	50 ± 10	162
Du Pont LTCC	145	1.6×10^{-2}	4.6	44	75 ± 10	141
Al_2O_3	445	1.1×10^{-2}	10.5	38	125 ± 10	124

The results indicate the diffusion of the PbO from the PZT layers into the LTCC substrate and, more significantly, the diffusion of the SiO_2 from the LTCC into the PZT during the firing of the thick-film structures.

The analysis of the darker phase in the two-phase PZT layer (see microstructure in Fig. 4d) showed a high concentration of SiO_2 (12 mol.%), CaO (8 mol.%) and ZrO_2 (55 mol.%), and some PbO (15 mol.%), while the analysis of the lighter phase showed high concentrations of SiO_2 (16%), and nearly "normal" concentrations of PbO (45%), TiO_2 (20 mol.%) and ZrO_2 (18 mol.%). The results are summarised in Table 4. Note that the phases are micrometer and sub-micrometer in size, while 1 μm is the limit of the spatial resolution of the EDS analysis. For this reason it is probable that the signal is not taken just from the analyzed phase but also from the neighbouring phases. Therefore, these results should not be taken to represent exact compositions of the dark and the light phases. However, the analysis indicates that the silica reacts with the PZT forming low-permittivity lead-based silicates rich in zirconia and lowers the dielectric constant of the PZT layers.

Poisson's ratios and Young's moduli of the substrates, measured using a nano-indentation technique [18], are summarised in Table 5.

In Table 6 the electrical parameters, i.e., the dielectric permittivity, ε', the dielectric loss, tan δ, the remanent polarisation, P_r, the coercive field, E_c, and the piezoelectric constant, d_{33}, of the thick-film structures fired at 850 °C on alumina and LTCC substrates are presented. The hysteresis loops of the PZT films on the LTCC substrates and on the alumina substrates are shown in Fig. 5. The d_{33} values were calculated from the data in Tables 1 and 5. For comparison, the dielectric constant and the piezoelectric constant, d_{33}, of the bulk PZT 53/47 ceramic are around 1000 and around 230 pC/N, respectively [17]. The dielectric constants were around 100 on the ESL and around 150 on the Du Pont LTCC substrates, as compared to 450 on the alumina substrates. The dielectric losses are in all cases around 1%. The highest remanent polarisation of over 10 μmC/cm^2 was measured for films on the alumina substrates. The piezoelectric constants for the films on alumina are the same as calculated, i.e., 125 pC/N. For the thick films on the Du Pont and ESL LTCC substrates the measured d_{33} values are around half and one third of those calculated, respectively. The results show that the interactions between the PZT thick films and the LTCC substrates cause a deterioration in the electrical characteristics. The relatively low dielectric constants and d_{33} values of the thick films fired on LTCC substrates indicate the formation of phases with a low permittivity, which are due to the diffusion of silica from the LTCC substrates into the PZT layers during firing. However, the ferro and piezo characteristics of the films show that the interactions are more significant on the ESL LTCC substrates. Therefore, of both evaluated LTCC materials the Du Pont LTCC is more suitable for the described applications.

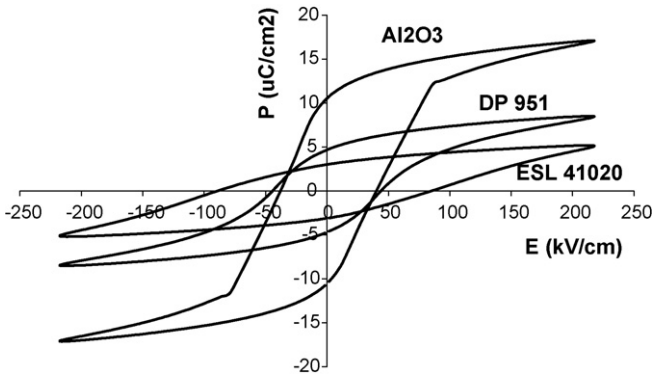

Fig. 5. Hysteresis loops of the PZT films on the LTCC and on alumina substrates.

4. Conclusions

The electrical and microstructural characteristics of $PbZr_{0.53}Ti_{0.47}O_3$ thick films with the addition of 6 mol.% PbO and lead germanate ($Pb_5Ge_3O_{11}$) on LTCC substrates were evaluated. Two LTCC tapes, i.e., Du Pont (DP) 951 and Electro Science Labs. (ESL) 41020 were selected. The ESL 41020 is a lead-free material, while the DP 951 contains between 2 and 3 mol.% of PbO. PZT films were also made on relatively inert alumina substrates. The results obtained with the alumina were used as a reference. Microstructures of the cross-sections of the resistors were investigated using SEM and EDS. The dielectric permittivities, dielectric losses, remanent polarisation, coercive field and piezoelectric constant, d_{33}, were measured.

The diffusion of PbO into the LTCC substrates and of the silica-rich phase into the PZT films was detected. The silica reacted with the PZT forming low permittivity lead-based silicates. This secondary phase diluted the ferroelectric PZT material, resulting in lower dielectric constants, remanent polarisations and piezoelectric constants. Better results, indicating less interaction, were obtained for the Du Pont LTCC substrates.

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