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PZT thick films on different ceramic substrates; piezoelectric measurements

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Abstract The piezoelectric, microstructural and electrical characteristics of thick PZT films on relatively inert alumina substrates and on two LTCC tapes, i.e., Du Pont 951 and Electro Science Labs 41020 were studied. A thick-film paste was prepared from the pre-reacted PZT powder ($PbZr_{0.53}Ti_{0.47}O_3$) and printed and fired on LTCC tapes and on alumina substrates, respectively. Dielectric permittivities, dielectric losses, remnant polarizations and coercive fields were measured. The dielectric constants (100–150) of thick films fired on LTCC substrates are low. The piezoelectric coefficients d_{33} were measured by different methods, i.e. Berlincourt piezometer, interferometry and piezoresponse force microscope (PFM). The d_{33} values on LTCC substrates are low (30–70 pm/V) as compared with values obtained on alumina substrates (around 120 pm/V). Lower dielectric constants and piezoelectric coefficients d_{33} of films on LTCC substrates are attributed to the formation of phases with a low permittivity due to the diffusion of silica from LTCC substrates into PZT films. The d_{33} constants of samples with different thicknesses of PZT layers (from 20 to 160 μm) at first increase with the increasing thickness of PZT layers and then decrease for thicker films. As the cracks in the structure were not observed the reason for the decreasing d_{33} values for thicker films is still unclear.

Keywords PZT thick films · Piezoelectric characteristics · LTCC

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1 Introduction

Piezoelectric ceramics are used in a wide range of sensors, actuators and transducers. Thick-film technology, i.e., the deposition of thick-film pastes by screen printing on ceramic substrates, is a relatively simple and convenient method for producing layers with a thickness in a range of few to 100 μm. The characteristics of thick-film ferroelectrics are similar to those of bulk materials [1–4]. The compositions of piezoelectric thick films are mostly based on $Pb(Zr_{1-x}Ti_x)O_3$ (PZT). The functional characteristics of the PZT depend on the ratio between Zr and Ti content in the PZT solid solution, but a rough estimation of the dielectric constant and the piezoelectric constant d_{33} for the compositions near the morphotropic boundary are 1,000 and over 200 pC/N, respectively. The substrates for thick PZT films are mainly alumina or silicon [5, 6]. However, LTCCs (low-temperature co-fired ceramics) have some advantages over alumina substrates: mainly a lower Young's modulus (alumina, 215–414 GPa; LTCC, 90–110 GPa [7, 8]), which is important for sensor and actuator applications. LTCC materials, which are sintered at the low temperatures typically used for thick film processing, i.e., around 850°C, are widely used for the production of MCM-Cs (Multi Chip Modules Ceramics) or MEMS (Micro Electro Mechanical Systems), especially for telecommuni-

cations and automotive applications. LTCCs are either based on crystallisable glass or a mixture of glass and ceramics [9–12]. To sinter it to a dense and non-porous structure at these, rather low, temperatures, it has to contain some low melting-point glass phase. This glass would interact with thick-film PZT layers, leading to changes in the electrical characteristics.

The processing temperature required to obtain dense PZT ceramics is around 1200°C, but this temperature is also not compatible with thick-film technology. To achieve processing temperatures between 800 and 900°C the basic compositions need to be modified with additives that form liquid phases at these temperatures. The sintering temperature can be lowered with low-melting point glasses, eutectics between low-melting point oxides or compounds with a melting point around or below 800°C e.g. $Pb_5Ge_3O_{11}$ [3, 13, 14].

Piezoelectricity is the property of some materials to develop a dipole moment when mechanical stress is exerted on them (direct effect). Similarly, applying an electric field to these materials produces a linearly proportional strain (inverse effect). In principle, both methods make it possible to measure the piezoelectric coefficient, d_{33}. If the direct effect is chosen then d_{33} is defined as

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

where

d_{33} is the piezoelectric coefficient (C/N),
D_3 is the component of dielectric displacement vector (As/m^2),
σ_3 is the component of the stress matrix (N/m^2)

and if the inverse effect is chosen then d_{33} is defined as

$$d_{33} = S_3/E_3, \tag{2}$$

where

d_{33} is the piezoelectric coefficient (m/V),
E_3 is the component of electric field vector (V/m),
S_3 is the component of the strain matrix.

However, for a measurement of the piezoelectric properties of thin and thick films one has to keep in mind that the film is always 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]

$$d_{33}^{eff} = d_{33} - 2d_{31}\frac{\frac{v}{Y} + s_{13}^E}{\left(s_{11}^E + s_{12}^E\right)}, \tag{3}$$

where

d_{33} and d_{31} are the piezoelectric coefficients (C/N or m/V),
s_{13}^E, s_{11}^E, s_{12}^E are the elastic compliance coefficients at constant electric field (m^2/N),
v is Poisson's ratio of the substrate,
Y is Young's modulus of the substrate (N/m^2).

Since for most materials $d_{31}<0$, $s_{13}<0$ and d_{31} is relatively large, the measured coefficient in films is smaller than in unclamped materials $\left(d_{33}^{effective} < d_{33}\right)$.

In this paper an investigation of the piezoelectric properties of PZT thick films on alumina and LTCC substrates is presented. The composition of PZT material was $PbZr_{0.53}Ti_{0.47}O_3$ (PZT 53/47), which is near the morphotropic phase boundary in the Pb(Zr, Ti)O_3 solid solution. The PZT films of different thicknesses screen-printed and fired on alumina substrates were also prepared.

The piezoelectric coefficients d_{33} were measured by different methods, i.e. Berlincourt piezometer, interferometry and piezoresponse force microscope (PFM). The Berlincourt piezometer measures the direct effect (see Eq. 1), while the other two methods measure the inverse effect (see Eq. 2). The Berlincourt piezometer measurement method is an improved normal load method. This method relies on the piezoelectric response, i.e. generated electrical charge is generated due to a mechanical load of the sample. The sinusoidally varying force is used, which is applied to the sample in the direction of polarization [17]. The sample is pre-loaded with a constant force of approximately 10 N to hold a sample in place.

The interferometry method is based on a single-beam optical interferometer, which detects micro-displacement of the moving surface of the sample. The laser beam is separated into two equal beams. The object beam is directed to the sample surface and reflected back to the beam-splitter. It recombines with the reference beam and produces an interference pattern on the detection plane. The interferometer intensity change is linearly proportional to the sample surface displacement due to the applied voltage [17].

An atomic force microscope (AFM) can be employed for the characterization of the inverse piezoelectric effect of materials. Usually the name piezoresponse force microscopy (PFM) is used for this type of measurement.. Measurement of piezoelectric displacements by PFM in contact mode can be made in two different ways: measurements of piezoelectric films by applying a voltage between a conducting tip and a bottom electrode or measurements by applying a voltage between the bottom and the top electrodes (in this case the tip is used just for detection of surface vibration) [18]. In both cases, a lock in amplifier is used to extract the tip deflection at a particular frequency.

The aim of this work is twofold; firstly to measure the piezoelectric characteristics of PZT thick films on relatively inert alumina substrates and on reactive LTCC substrates, and secondly to evaluate the dependence of the piezoelectric coefficients on thickness of PZT layer.

2 Experimental

The $PbZr_{0.53}Ti_{0.47}O_3$ (PZT 53/47) composition, which is at the morphotropic boundary, 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% (Aldrich 21,190-7), ZrO_2 99% (Tosoh TZ-0), and TiO_2 99% (Alfa–Johnson Matthey 042681). To this was added 2 wt% of lead germanate, with the composition $Pb_5Ge_3O_{11}$ (melting point 738°C) as a sintering aid. Lead germanate (PGO) was also prepared by mixed-oxide synthesis from PbO and GeO_2 99% (Ventron 34104) at 700°C. After the synthesis, both compositions were ball milled in acetone for 1 h and dried. A thick-film paste was prepared from the PZT (2% PGO) and an organic vehicle (ethyl cellulose, alpha-terpineol and butil carbitol acetate) by mixing on a three-roller mill.

Samples were printed and fired on +99% Al_2O_3 (alumina), and two different low temperature ceramics (LTCC) substrates; Electro Science Labs. (ESL) 41020 and Du Pont 951. The LTCC 41020 is a lead-free material, while the LTCC 951 contains between 2 and 3 mol% of PbO. The thickness of green and fired single tapes are 254 and 200 μm, respectively, for Du Pont 951, and 120 and 100 μm, respectively, for ESL 41020. The LTCC substrates were made by laminating three layers of LTCC tape at 70°C and a pressure of 20 MPa. The green tapes were fired for 1 h at 450°C (organic binder burnout) and 15 min at 875°C.

Capacitors were used as test structures. Test structures were printed with a pattern consisting of 16 capacitors. A picture of the test pattern is shown in Fig. 1. A thick-film gold paste (ESL) was printed on the substrates and fired at 850°C. The PZT paste was printed twice and fired at 850°C and again printed twice and fired at the same temperature. Gold electrodes were then printed and fired on the PZT film. The thickness of the fired PZT layers, which was around 50 μm, was measured with Viking optical profiler system, with a high-resolution non-contact Nobis sensor based on confocal chromatic technology. For samples on alumina with different thicknesses of PZT layer the same method was used, i.e. printing of two layers and firing, and then repeating this procedure until the required thickness was obtained.

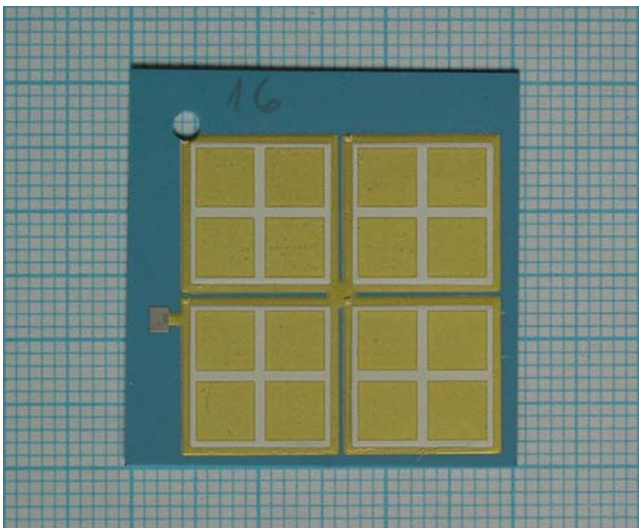

Fig. 1 A picture of the test pattern (mm grid)

Table 1 The electrical parameters of the PZT thick films fired at 850°C on LTCC and alumina substrates, respectively.

Substrate	ε (at 1 kHz)	$\mathrm{tg}\delta \times 10^{-2}$ (at 1 kHz)	P_r ($\mu C/cm^2$)	E_c (kV/cm)
LTCC 41020	105	0.7	3.0	85
LTCC 951	145	1.6	4.7	44
ALUMINA	445	1.1	10.5	40

For the microstructural investigation some samples prepared on alumina ceramics 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 a LINK ISIS 300 energy-dispersive X-ray analyser (EDS) was used for the 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.

The dielectric permittivity and dielectric losses were measured with an HP-4284 Precision LCR Meter at 1 kHz. The samples of 50 μm thickness were polarized in a silicon-oil bath at 100°C with a continuously applied electrical field of strength 100 kV/cm for 20 min. The PZT thick films with different thicknesses were polarized with an electrical field of strength 50 kV/cm for 20 min. The piezoelectric responses of the samples were measured by different methods as described in the Introduction. The Berlincourt piezoelectric measurements were made at a frequency of 100 Hz.

For PFM measurements an atomic force microscope (Digital Instruments) was used. A Silicon tip coated with a 20 nm thick platinum/iridium layer was employed. The measurement was made by applying an increasing voltage from 0 to 4 V between the conducting tip and the bottom electrode. The noise level of measurement was around 1 pm/V and it was determined by mechanical precision of the system and by the noise level of the electronics. A different type of PFM measurement was also made by applying the voltage at different frequencies between the top and the bottom electrodes of the piezoelectric sample. In this case the non-conducting uncoated Si tip was placed on the top electrode for the detection of local vibrations of the sample surface induced by the AC signal. For the

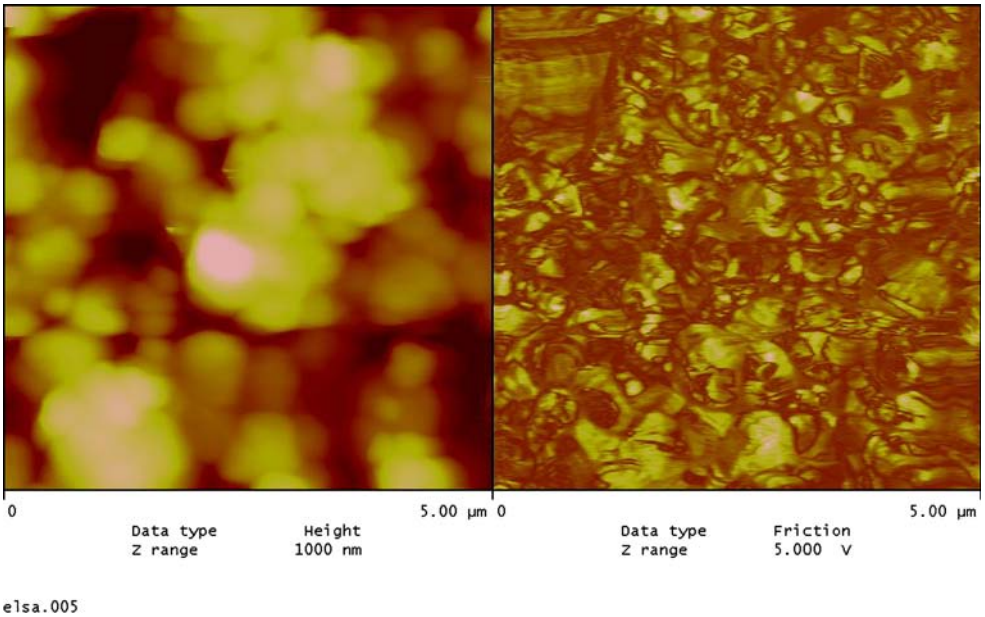

Fig. 2 Topography (*left*) and the vertical PFM (*right*) images from a PZT 50 µm thick film obtained with a Pt/Ir-coated AFM tip

interferometry method, an interferometer designed Interferomet Ltd. and NPL was used. The light source was He–Ne laser with a wavelength of 632.8 nm. The electric field was again applied between the top and the bottom electrodes and measurements were made at 5 V.

3 Results and discussion

In Table 1 the electrical parameters, i.e., the dielectric permittivity ε; the dielectric loss tgδ; the remnant polarisation P_r; and the coercive field E_c; of the 50 µm thick films on alumina and LTCC substrates are presented.

The relatively low dielectric constants of the thick films fired on the LTCC substrates indicate the formation of phases with a low permittivity, mainly PbO–SiO_2 based glassy phase, which is presumably due to the diffusion of silica from the LTCC substrates into the PZT layers during firing. The PbO rich phase also diffuses from PZT layer into LTCC substrate [19, 20]. The dielectric constants of films on alumina are roughly half of the values for the bulk ceramics. The dielectric losses are around 1%, which is comparable with bulk values.

In the AFM image of the surface from a PZT 50 µm thick film on LTCC (ESL) substrate obtained with a Pt/Ir-coated AFM tip is presented in the Fig. 2. The lateral image is on the left and the vertical PFM image is on the right. The lateral image indicates a rough surface with grain sizes approximately 1 µm in size. The image quality is poor, in part due to the large variation in height across the film. The PFM image gives an indication of the out of plane piezoelectric coefficient of the film. Structure is observed, indicating the presence of multidomains within each grain. The data shows variation in the out of plane piezoelectric coefficient, both within a grain and across the film surface.

The piezoelectric coefficients d_{33} of the thick PZT films on alumina and LTCC substrates were measured with different techniques and equipment i.e.: Berlincourt piezometer, interferometer and PFM. As mentioned before, the Berlincourt method measures the direct effect while other two methods measure the indirect effect. Results are presented in Table 2. The measured effective d_{33} piezo-

Table 2 A comparison of d_{33} measured for 50 µm thick PZT films on two different LTCC (ESL 41020 and Du Pont 951) and on alumina substrates.

Substrate	Berlincourt piezometer 100 Hz (pC/N)	Interferometer 3–4 kHz (pm/V)	PFM conducting Si tip 15–30 kHz (pm/V)	PFM non conducting Si tip 5–45 kHz (pm/V)	d_{33}^{eff} (calculated) (pC/N)
LTCC 41020	50	25	29	25	162
LTCC 951	75	40	38–42	33	141
ALUMINA	125–130	125	119–123	/	124

The values were measured by Berlincourt method, by laser interferometry and by PFM. The films were polarised with the field of 100 kV/cm.

Table 3 Piezoelectric coefficients for the PZT composition.

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

electric coefficients were compared with values calculated by Eq. 3. The constants used for the calculations are presented in Table 3 for the PZT material [21] and in Table 4 for alumina and LTCC substrates [22].Young's moduli of the substrates were measured by nano-indentation technique (ASTM Standard C 1161–90).

The measured d_{33} values of PZT films on alumina are nearly the same as calculated values. These results indicate that there are no significant reactions between PZT films and alumina substrates, which could lead to a deterioration in piezoelectric characteristics. The relatively low d_{33} of the thick films on the LTCC substrates indicate the formation of non-piezoelectric phases, which are due to the diffusion of silica from the LTCC substrates into the PZT layers during firing. For LTCC substrates the values obtained by both indirect methods are comparable. The Berlincourt method yields higher d_{33} values. However, data from the literature indicate that the Berlincourt method, has a relatively low reliability and relatively low resolution. Indirect methods, for example interferometry, are more reliable [17]. However, the Berlincourt method is widely used because it is simple and direct.

The d_{33} values of PZT thick films with different thicknesses on alumina substrates were measured by the PFM. The results are presented in Fig. 3. For similar film thicknesses of samples polarized with 100 kV/cm (Table 2) and with 50 kV/cm (Fig. 3) the measured d_{33} values are around 125 pm/V and around 100 pm/V, respectively. This is presumably due to a more complete polarization with the higher electric field. The dashed line between measured values is just a guide to the eye. The d_{33} values at first increase from 75 pm/V to around 100 pm/V and than significantly decrease with increasing thickness to 40 pm/V at 160 μm. Hypothetically, some reasons for this could be either cracks in the microstructure or an increased porosity in thicker films. Microstructure of 80 μm thick PZT film is shown in Fig. 4. The PZT film is a single-phase solid solution with pores ranging from less than 1 μm up to nearly 10 μm. Cracks in the structure were not observed and the microstructures of thinner and thicker films are similar. Therefore, the reason for the decrease of d_{33} with increasing thickness is still under investigation.

Table 4 Poisson's ratios and Young's moduli of the alumina and LTCC substrates.

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

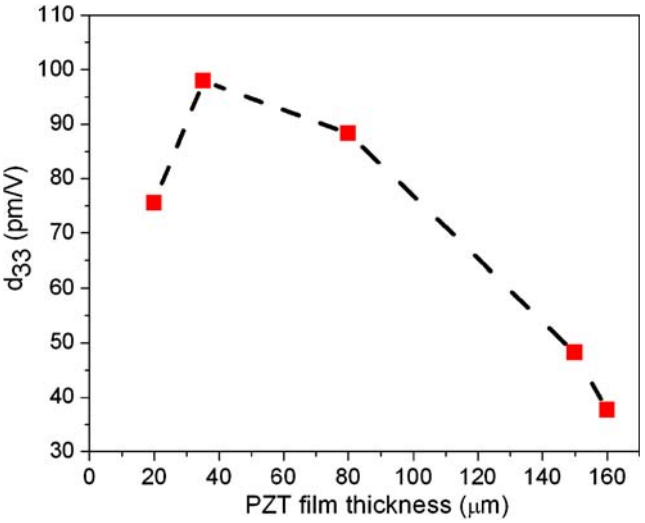

Fig. 3 Average PFM measurements of d_{33} for the samples with different thicknesses of the PZT film. The polarizing field was 50 kV/cm

4 Summary

Dielectric permittivity, dielectric losses, remnant polarisation and coercive field were measured. The relatively low dielectric constants (100–150) of thick films fired on LTCC substrates were attributed to the formation of phases with a low permittivity which are due to the diffusion of silica from LTCC substrates into PZT films during firing. The piezoelectric coefficients d_{33} were measured by different methods, i.e. Berlincourt piezometer, interferometry and PFM.

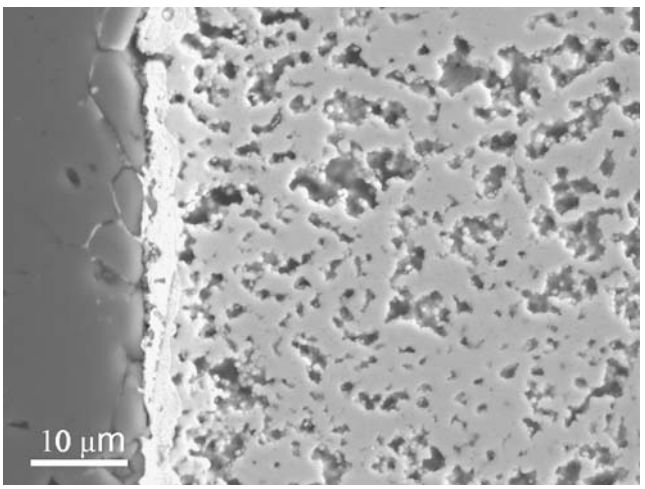

Fig. 4 Microstructure of 80 μm thick PZT film fired on alumina. The substrate is on the *left*

The measured d_{33} values of PZT films on alumina are comparable with calculated values while the values on LTCC substrates were lower. The results obtained on LTCC substrates are due to the formation of non-piezoelectric phases. The reason is mainly the diffusion of silica from the LTCC substrates into the PZT layers. For LTCC substrates the values obtained by both indirect methods were comparable while the values obtained with the Berlincourt are higher.

The d_{33} constants of samples with different thicknesses of PZT layers (from 20 to 160 μm) were measured with PFM. Measured d_{33} values at first increase with increasing thickness of PZT layers and then significantly decrease for thicker films. As the cracks in the structure were not observed and the microstructures of thinner and thicker films were similar the reason for the decreasing d_{33} values for thicker films is still unclear. Further work to investigate these variations is continuing.

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