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PZT and PT screen-printed thick films

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Abstract

Thick films (40–80 μm) of modified lead zirconate titanate (PZT) and lead titanate (PT) are screen-printed on alumina substrates electroded with Ag–Pd. First the influence of the powder grain size distribution on film characteristics after sintering is studied. With regard to the powder preparation, two processes are used: a mixed-oxide method and a wet coprecipitation process. Then thick films characteristics are compared with bulk ceramics ones. Two main factors explain the observed differences: residual porosity of the film and lateral clamping effect of the substrate. Other piezoelectric and elastic films coefficients are estimated from a plane wave model. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Films; Grain size; Piezoelectric properties; PT; PZT

1. Introduction

Ferroelectric ceramic materials are used for various electronic applications: sensors, actuators, motors, etc. Applications of PZT depend on its characteristics.[1] With a dopant combination of Mn, W and Sn, the PZT composition gives a permittivity $\varepsilon_r = 2000$ and a piezoelectric coefficient $d_{33} = 400$ pC/N. PT modified with Calcium shows a low permittivity and a large electromechanical anisotropy.[2] It may be useful in non destructive testing.

Piezoelectric applications in micro-devices require films with thickness inferior to 100 μm. Instead of machining down and bonding bulk ceramics, a solution is to manufacture screen-printed thick films deposited directly on substrates. The present investigation is devoted to the study of PZT and PT films on alumina. First the importance of starting powder type and grain size distribution on the quality and the characteristics of thick films is shown. For a better understanding of the films' properties, they are compared to bulk ceramic values. In order to estimate other elastic and piezoelectric coefficients, the experimental results obtained on films are introduced in a plane wave model which takes into account bulk ceramics properties and influence of substrate and electrodes.

2. Experimental

The two investigated compositions are $Pb_{0.93}Sr_{0.07}(Zr_{0.455}Ti_{0.445}W_{0.036}Sn_{0.036}Mn_{0.028})O_3$ and a lead titanate modified with 28 mol% Ca in order to obtain the optimal ratio (k_t/k_p). Powder synthesis is achieved by the conventional mixed oxides method (dry method: DM): mixing of oxides or carbonates, calcining at 950°C for 6 h and milling. For PZT, a coprecipitation process (wet method: WM) is also employed.[3] Tetra-*n*-butyl titanate, tetra-*n*-butyl zirconate and acetates or chlorides of cations occupying the B site are dissolved in a solution of oxalic acid. Acetates of A site cations are added to this mix. After stirring, hydroxides and oxalates are precipitated by addition of ammonia. The product is calcined at 600°C for 10 h. Grain size distribution is controlled by a laser Coulter LS130 granulometer and a Monosorb Quantachrom (based on BET theory). Bulk ceramics are obtained by sintering pressed disks at 1100°C (PT) or 1250°C (PZT) for 3 h. Then samples are poled in oil under 6–7 kV/mm (PT) or 3–4 kV/mm (PZT).

Thick films are manufactured by screen-printing an ink on a substrate.[4–6] Ink is prepared from the piezoelectric powder and an organic part made of dispersing agent (BEEA: buthoxyethoxy-ethyl acetate), solvent (α-terpineol), binder (PVB: polyvinyl butyral) and plasticizer (PEG: polyethylen glycol). Optimized formulations are given on Table 1.

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Table 1
Formulations (in mass%) according to the powder type and the synthesis routes

	DM PZT	WM PZT	DM PT
Powder	85	80	70
BEEA	3.7	4.9	7.3
Terpineol	7.5	10.0	15.1
PVB	1.6	2.1	3.1
PEG	2.2	3.0	4.5

Films are screen-printed on 96% alumina substrates ($25\times12\times0.250$ mm^3; Rubalit 708S, Ceramtec) on which a Ag–Pd paste (4075 Dupont de Nemours) was previously deposited and fired at 850°C. The PZT films are dried at 120°C, fired at 500°C and sintered in a belt furnace at temperatures from 950 to 1030°C for 6–20 min (25 min heating ramp and 15 min cooling down). Some tests are made by applying an uniaxial pressure from 100 to 200 MPa using a hydraulic press on dried films. Some results are given for double layers: the precedent operations are repeated twice. After sintering Ag (7315 Cerdec) electrodes are deposited on top of the films. Polarisation is carried out in oil with 10–12 kV/mm (PT) and 6–10 kV/mm (PZT) at 80°C (PT) and 120°C (PZT).

The permittivity is measured with a HP 4284A apparatus, and the d_{33} coefficient with a Berlincourtmeter. The resonance frequencies are determined with an impedance analyser HP 4194A. The d_h coefficient is obtained from measurements of the charge release when the samples are submitted to a hydrostatic pressure of 1 MPa.

3. Results and discussion

3.1. Influence of the starting powder type

In order to obtain a suitable screen-printing ink, the powder percentage in ink must be adjusted according to the type and size distribution of the particles. DM PZT has an uniform distribution of particle size (Fig. 1) and a small specific surface area S_{sp} (Table 2). The powder content in ink is 85 mass%. WM PZT shows a bimodal distribution. The mean particle size is similar to the DM one whereas the modal value (which occurs most frequently) is smaller. Its S_{sp} is determined to be 5.7 m^2/g. The first peak on the curve corresponds to the single particles and the second population seems to be agglomerates. Because of the wet synthesis and a 600°C temperature calcination grains are fine as proved by a high S_{sp}, so interaction forces between particles are important, consequently they adhere together to form agglomerates very hard to break. Therefore ink homogenizing becomes difficult, the powder amount must be decreased, but it is possible to obtain an homogeneous ink by using a triple roll mill during ink elaboration.

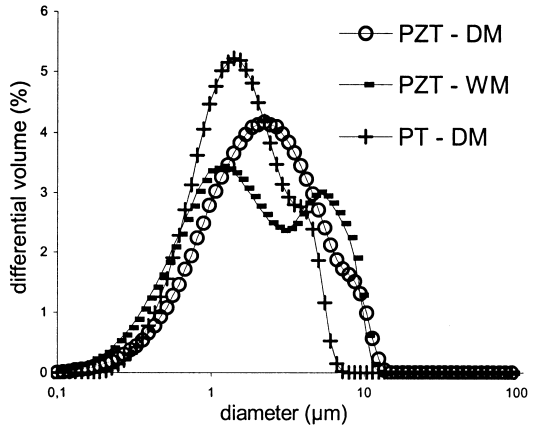

Fig. 1. Grain size distribution of PZT and PT powders according to the different synthesis routes.

Table 2
Volume granulometry characteristics for the different powders and influence on ink formulation

	DM PZT	WM PZT	DM PT
Mean (µm)	2.2	1.9	1.6
Median (µm)	2.2	1.8	1.6
Mode (µm)	2.3	1.2	1.5
S_{sp} (m^2/g)	1.1	5.7	3.1
Powder in ink (%)	85	80	70

The distribution of DM PT powder is uniform with a specific surface of 3.1 m^2/g. The maximum powder amount (70 or at most 75 mass%) is lower than for WM PZT case.

3.2. Characterization of PZT and PT thick films and bulk ceramics

The Curie temperature estimated on thick films (TF) and bulk ceramics (BC) are similar (Table 3): there's no significant difference in the composition. WM TF gives enhanced values compared to DM TF, the sintering temperature is decreased to 1000°C because of smaller particles and even a 950°C temperature gives good results. For PZT, about 1/3 of permittivity and d_{33} bulk values is obtained for films whereas PT TF show excellent properties (Table 3). From Banno's investigations[7] who has developed for 0-3 composites a theory applicable to porous materials, the following equations have been determined to explain the observed differences, first between TF and BC and second between PZT and PT films:

$$\varepsilon_{33F} = \varepsilon_{33}\left(1 - p - p^{2/3}\left(1 - p^{1/3}\right)n\right)\left(1 - \alpha k_p^2\right) \quad (1)$$

$$d_{33F} = (1-\alpha)d_{33} + \alpha d_{33}\left[1 - \frac{2s_{31}^E d_{31}}{\left(s_{11}^E + s_{12}^E\right)d_{33}}\right] \quad (2)$$

Table 3
Experimental characteristics of PZT and PT thick films (TF) and bulk ceramics (BC)

	PZT				PT		
	DM TF	pressed DM TF	WM TF	BC	DM TF	pressed DM TF	BC
Sintering (°C)	1030	1030	1000	1250	1030	1030	1100
Thickness (mm)	0.070	0.060	0.060	0.8	0.065	0.050	0.8
Density (g/cm^3)	4.5–5.5	6.0–6.5	4.5–5.5	7.3	3.5–4	4.5–5	6.5
T_c (°C)	212		208	220	260		248
k_p				0.60			0.04
k_t				0.53			0.52
ε_r	600	800	750	2100	135	180	200
d_{33} (pC/N)	110	100	130	410	50	50	62
d_h (pC/N)	26		33	46	21	31	49
$-d_{31}$[a] (pC/N)	42		48	182	14	10	6
$-d_{31}$[b] (pC/N)				170			2

[a] Calculated from the formula: $-d_{31} = (d_{33} - d_h)/2$.
[b] Measured on a rectangular sample.

where p is the film porosity, α the clamping amount and n a pores shape factor as defined in Refs. 5 and 7. For PT, lateral effects are negligible because the transverse piezoelectric coefficient d_{31} and the planar coupling factor k_p are very low. Experimental d_{33} values for TF and BC are not very different, as confirmed by relation (2). The permittivity is lower: it is in good agreement with relation (1) because ε_r depends directly on porosity. For PZT, both ε_r and d_{33} are lower because of two factors effects: porosity and lateral clamping to the substrate which is largely superior to PT one because of a large k_p value.

The lateral clamping depends on substrate nature and material characteristics but the porosity can be decreased by applying an uniaxial pressure: as shown in Table 3, layer thickness is decreased, density and consequently permittivity of films are increased. Contrary to PT films, PZT value of permittivity remains relatively low despite the density improvement, certainly because of the substrate clamping.

Hydrostatic coefficients d_h are determined and used to calculate d_{31}. For comparison, rectangular BC samples are made to measure directly the transverse coefficient (Table 3). The two methods give similar results. d_h and d_{31} PZT values are lower for TF than for BC, certainly because of the lateral clamping of the substrate. For PT, even if the d_{33} is nearly the same for TF and BC, only the half bulk d_h is measured for films. Two assumptions can be made: first, the substrate has an influence even if the lateral effect is negligible; second, the residual porosity of the layer plays a role. The second assumption is verified: for a pressed sample, i.e. for a reduced porosity, d_h value enhances from 21 to 31 pC/N.

3.3. Evaluation of other coefficients with a plane wave model

Primarily, a plane wave model was developed which took into account the three layers: piezoelectric layer, electrodes and substrate, but it is difficult to estimate the electrodes characteristics, principally thickness (lack of precision, diffusion into alumina) and consequently density, so the choices of propagation velocity and acoustic impedance values become complex. Consequently, a two layers model is studied: one layer for the active material (index 0) and the other which is constituted of substrate and electrodes (index SE).

Resonance frequencies in the thickness mode are given by the expression (3):

$$Z_0^D \tan\frac{w l_0}{V_0^D} + Z_{SE}\tan\frac{w l_{SE}}{V_{SE}} = 0 \tag{3}$$

where l, V and Z are, respectively, thickness, propagation velocity and acoustic impedance.

Because of the strong residual porosity of the film, BC characteristics (index *) must be modified. The TF density is $\rho_0 = \rho_0^* x$ where x is defined as $x = 1 - p$. Empirical expressions[8,9] have been used to write a relation between TF and BC elastic stiffness:

$$c_{33}^E = c_{33}^{E*} x^{2.8} \tag{4}$$

Consequently:

$$V_0^D = V_0^{E^*} x^{0.9}\left(1 + bx^{2.8}\right)^{0.5} \text{ with } b = \frac{d_{33}^2 c_{33}^{E*}}{\varepsilon_{33}^S} \tag{5}$$

$$Z_0^D = Z_0^{E^*} x^{1.9}\left(1 + bx^{2.8}\right)^{0.5} \tag{6}$$

The ε_{33}^S clamped permittivity is measured in the high frequency range (30–40 MHz). Eqs. (5) and (6) are reported on (3), so x can be calculated. SE layer values (calculated with alumina characteristics and modified by experimental measurements which take into account the electrode thickness), BC PZT and PT characteristics are

Table 4
Characteristics of the bulk piezoelectric materials and the SE (substrate + electrode) layer[a]

	SE layer	Bulk PZT	Bulk PT
ρ (kg m^{-3})	3746	7340	6450
V (ms^{-1})	9527	4093	4413
Z (Mrayls)	35.7	30.02	28.46
c_{33}^{E}* (10^{10} N m^2)		12.29	12.56

[a] Thickness l = 250 + 20 μm.

Table 5
Elastic and piezoelectric coefficients calculated from the plane wave model for PZT and PT thick films

	PZT film	PT film
F_p (Mhz)	9.9875	10.463
l_0 (10^{-6} m)	66	63
d_{33} (pC/N)	129	49
ε_{33r}^{S}	650	102
x	0.63	0.59
ρ_0 (g cm^{-3})	4.52	3.73
k_t	0.29	0.26
c_{33}^{E} (10^{10} N m^{-2})	3.17	2.71
c_{33}^{D} (10^{10} N m^{-2})	3.46	2.91
V_0^{E} (m s^{-1})	2766	2792
Z_0^{E} (Mrayls)	12.5	10.4
e_{33} (C m^{-2})	4.09	1.33
h_{33} (10^8 C m^{-1})	7.11	1.47

given in Table 4. Table 5 presents results of model calculations. Experimental and calculated densities are similar. Thickness coupling factors are more than half bulk values. Concerning elastic coefficients, they are largely inferior for films.

4. Conclusion

PZT and PT thick films elaboration and characterization are described. The grain size distribution is an important factor which provides the optimal powder percentage that can be incorporated in ink. Powder synthesis has a strong influence: a coprecipation process allows to obtain fine grains and enhances piezoelectric properties.

The differences between thick films and corresponding bulk ceramics values are explained by two main factors: residual porosity which can be decreased by applying an uniaxial pressure and lateral clamping due to the substrate. Morever the influence of clamping is higher for PZT which has a large k_p than for PT which has a very low one.

The interest of the plane wave model which has been developed is to provide approximate films coefficients values. It requires further improvements, in particular for the determination of the electrodes characteristics.

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