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Processing and Characterization of $PbTiO_3$ Thick Films on Alumina Substrates

L. SIMON,[1] S. LE DREN,[2] P. GONNARD[1] & G. PIERRE[3]

[1]*Laboratoire de Génie Electrique et Ferroélectricité, INSA de Lyon, Bat. G. Ferrié 8, rue de la Physique, 69621 Villeurbanne Cedex, France*

[2]*Framatome—Centre technique—Site industriel Châlon/Saint-Marcel, BP13—71380 Saint-Marcel, France*

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Abstract. Calcium modified lead titanate (PT) thick films (thicknesses from 50 to 130 μm) are deposited by screen-printing on alumina substrates. First, the influence of the Ca-doping process and of the grain size distribution on the film quality and the piezoelectric coefficients is studied. The permittivity and charge coefficient d_{33} values of the films are compared with bulk ceramics ones. The consequences of very low coupling planar factors for PT are discussed. Piezoelectric and elastic properties are calculated with the help of a plane wave model which takes into account the three layers: substrate, electrodes and PT layer.

Keywords: thick films, piezoelectric, lead titanate, screen-printing, characterization

1. Introduction

Lead titanate (PT) is often used in high frequency and high temperature devices, because of both a high Curie temperature and a low permittivity. PT modified with a large amount of calcium, shows a large electromechanical anisotropy: the piezoelectric effect in the poling field direction is larger than in the perpendicular one [1, 2]. The optimal ratio (k_t/k_p) is obtained with a 28 mol% Ca content. An application of these materials is on non destructive testing (NDT) [3].

In order to work in the high frequency region, it may be interesting to manufacture thick films in order to eliminate ceramics machining and bonding steps, with the possibility of using different substrates.

This paper presents powder investigation, screen-printing of thick films on alumina substrates, film characterization and comparison of some coefficients with bulk ceramic values.

2. Experimental Procedures

2.1. Powder and Ceramics

PT powder is prepared following the solid process, by firing a mixture of oxides and/or carbonates at high temperature. Raw materials include PbO, TiO_2, CaO or $CaCO_3$ and some other dopant oxides. They are mixed together in a wet ball mill for 2 h. Calcining is achieved at 900 or 950°C for 10 h with a heating rate of 3°C/min. Then the powder is ground for 3 h.

Grain size distribution is controlled by a Laser Coulter LS130 granulometer. The specific surface area (from BET theory) is measured with a Monosorb Quantachrom.

After addition of a binder, samples are pressed and sintered at different temperatures (1050 to 1200°C) for 3 h with a 2°C/min heating rate. Disks of 10 mm in diameter and 0.6–0.8 mm in thickness are machined and coated by a screen-printed Ag top electrode. Then samples are poled in a silicon oil bath at 120°C under 6 to 7 kV/mm dc fields.

2.2. Ink and Thick Films

Ink is obtained by mixing the active powder with an organic vehicle, made of a dispersing agent (Butoxy Ethoxy Ethyl Acetat: BEEA), a binder (Poly Vinyl Butyral: PVB), a solvent (α-terpineol) and a plasticizer (Poly Ethylen Glycol: PEG) [4, 5]. The percentages of these components must be adjusted in order to obtain an ink suitable for screen-printing, i.e.

Table 1. Formulations of *A* and *B* inks (percentage by mass).

Formulation (%)	*A*	*B*
PT powder	70	80
Dispersing agent	7.3	4.9
Solvent	15.1	10.0
Binder	3.1	2.1
Plasticizer	4.5	3.0

with good spreading properties and a correct viscosity. Two formulations given on Table 1 are finally selected.

96% alumina substrates ($25 \times 12 \times 0.25$ mm^3) are electroded with an Ag-Pd paste and fired at 850°C for 1 h. Ink is deposited by hand-driven screen-printing [6, 7]. Such a simple method leads to thicknesses from 10 to 200 μm. The thickness depends on ink viscosity (percentage and type of powder), on sieves: 3 types with decreasing mesh are used: 12T (T_1), 17T (T_2), 27T (T_3) where the number before T represents the number of wires per centimeter. The numbers in parenthesis correspond to mean thicknesses measured on several samples.

Samples are then dried at 60°C, fired at 500°C for 5 h with a heating rate of 1°C/min to remove the organic components and sintered at temperatures between 1000 and 1100°C. Two sintering processes are used: flash sintering (FS), samples are quickly introduced in the furnace then are taken out after a hold time of 5 to 15 min and cooled down in air; rapid sintering (RS) made in a belt furnace with a 25 min heating ramp, a 10–20 min hold time and a 15 min cooling down. After sintering, Ag top electrodes are deposited. Thick films are poled in a 80°C oil bath with 10 to 15 kV/mm dc fields.

2.3. Characterization

Densities are estimated from the mass and volume measurements in air. The dielectric losses (tgδ) and the permittivity (ε_r) are measured at low voltage (1 V, 1 KHz) with a HP 4284A apparatus. The charge constant d_{33} is measured at 100 Hz with a Berlincourtmeter (Channel Products Inc). The series resonance (maximum of conductance G) and the parallel resonance (maximum of resistance R) of the thickness mode are determined with an impedance analyser HP4194A. These values allow the calculation of the electromechanical coefficients of the bulk ceramics.

In order to evaluate the other piezoelectric coefficients of the films, a plane wave model with 3 layers is developed: the active layer (0), the electrode layer (1) including the upper and lower electrodes, the alumina substrate layer (2). The parallel resonance frequencies ($f_p = w/2\pi$) are given by the following relation:

$$\tan\frac{wl_0}{V_0^D}\tan\frac{wl_1}{V_1}\tan\frac{wl_2}{V_2} - \frac{Z_0^D}{Z_1}\tan\frac{wl_1}{V_1} - \frac{Z_0^D}{Z_2}\tan\frac{wl_2}{V_2} - \frac{Z_0^{D^2}}{Z_1Z_2}\tan\frac{wl_0}{V_0^D} = 0 \quad (1)$$

where l_i, V_i et Z_i are respectively thickness, propagation velocity and acoustic impedance.

The thick film density is $\rho_0 = \rho_0^* x$ where x is defined as $x =$ (1-porosity) and ρ_0^* is the density of the bulk PT. Empirical expressions [8] have been used to write a relation between the elastic stiffness of the film (c_{33}^E) and of the bulk (c_{33}^{E*}):

$$c_{33}^E = c_{33}^{E*} x^{2.8} \quad (2)$$

Consequently following the standards equations of piezoelectricity and assuming $d_{31} \approx 0$ in PT one obtains:

$$c_{33}^D = c_{33}^{E*} x^{2.8}\left(1 + b c_{33}^{E*} x^{2.8}\right) \quad (3)$$

where $b = \frac{d_{33}^2}{\varepsilon_{33}^S}$ is calculated from the d_{33} value and the permittivity ε_{33}^S measured in the high frequency range (≈40 MHz).

$$V_0^D = \left(\frac{c_{33}^D}{\rho_0}\right)^{1/2} \quad (4)$$

$$Z_0^D = \rho_0 V_0^D \quad (5)$$

Equations (3–5) are substituted into (1) so x can be calculated as well as the elastic stiffness of the film. Then the thickness coupling factor k_t, the e_{33} and h_{33} coefficients can be derived.

3. Results and Discussion

3.1. Powder Investigations

Table 2 and Fig. 1 give the granulometric characteristics of four PT powders prepared following different routes.

O900 has a very uniform distribution. With this powder, ink homogenizing is very easy but the powder percentage is limited to 70 because of too small particles. For $CaCO_3$ based compositions (C900, GC900 and C950), ink elaboration is more difficult. With powder C900, the grains are fine (see modal value corresponding to the top of the granulometry curve and specific surface on Table 2) with agglomerates around 6 μm. A carbonate grinding (mean grain size decreased from 15 to 5 μm) is better for the final distribution (GC900), probably due to an improved reaction during calcining. By enhancing reaction temperature (C950), a totally unimodal repartition is observed (Fig. 1) with a larger mean grain size. Then with C950 the powder amount in the ink can be increased up to 80%.

For each of these powders, optimization of sintering and poling conditions made on bulk ceramics leads to results given on Table 3.

3.2. Optimization of Thick Films Made with CaO Based Powder

Table 4 shows the influence of the sintering conditions on permittivity and piezoelectric coefficient for thick films prepared from the O900 powder. A/1C/T2 means an A formula ink, with one coating (1C) and a T2 sieve. The best piezoelectric characteristics are obtained with a 1050°C—10 min sintering. Similar results are obtained with a double coating method (A/2C/T3).

3.3. Optimization of Thick Films Made with $CaCO_3$ Based Powder

As CaO can easily be hydrated with time, a good reproducibility of the results cannot be guaranteed. So

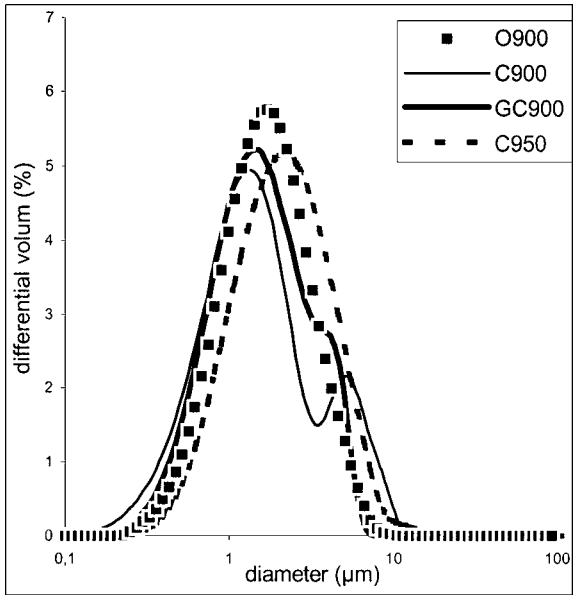

Fig. 1. Grain size distribution of PT powder for the four compositions.

$CaCO_3$ based powders are prepared: C900, GC900 et C950 (Table 2).

3.3.1. C900. C900 (A formula) gives poor grade results: because of the grain size distribution, ink homogenizing is very difficult, hence bad quality films and low piezoelectric results are obtained.

3.3.2. C950. Several tests with A and B inks and following different deposit conditions have been made (Table 5). C950-1 gives low permittivities. This result can be related to the powder granulometric distribution (Fig. 1). The uniform grain size repartition of the powder allows a suitable ink homogenizing. As the grain size is larger than O900 one, the powder percentage can be enhanced from 70 to 80 (C950-2, 3 et 4). Then piezoelectric results are in good agreement with O900 values. It can be noticed that

Table 2. The different powders and their granulometric characterisitics.

Reference	Introduction mode of calcium	Calcining temperature	Mean (μm)	Mode (μm)	Specific surface area (m^2/g)
O900	Oxyde CaO	900°C	1.69	1.76	2.73
C900	Carbonate $CaCO_3$	900°C	1.57	1.34	4.18
GC900	Grinded carbonate $CaCO_3$	900°C	1.59	1.47	2.61
C950	Carbonate $CaCO_3$	950°C	2.14	2.31	1.32

Table 3. Characteristics of the bulk ceramics obtained from the four powders.

	O900	C900	GC900	C950
Sintering T (°C)	1100	1100	1100	1150
ε_r	210	190	195	195
d_{33} (pC/N)	63	61	62	59
k_t	0.53	0.53	0.52	0.50

Table 4. Influence of the FS (flash sintering) conditions on permittivity and piezoelectric coefficient (O900).

Temperature (°C)/time (min)	ε_r	d_{33} (pC/N)
A/1C/T_2		
950/5	39	21
1000/5	63	31
1000/10	75	34
1000/15	91	38
1050/5	98	36
1050/10	130	48
A/2C/T_3		
1050/10 ($e = 55$–65 μm)	115–140	45–50

Table 5. C950 results obtained with a 1050°C—10 min FS according to deposit conditions and ink formula.

	e (μm)	Density (g/cm^3)	ε_r	d_{33} (pC/N)
C950-1 (A/2C/T_2)	80–95	3.5–3.8	70–80	44–50
C950-2 (B/1C/T_1)	125–135	3.5–3.8	115–130	45–51
C950-3 (B/1C/T_3)	50–65	3.2–3.6	110–135	40–49
C950-4 (B/2C/T_3)	160–200	3.1–3.7	100–130	43–50

the ink is more viscous and consequently more difficult to screen-print: sieve mesh is visible on the film surface. This phenomenon is still more pronounced for the second deposit. For C950-4, several crossings are sometimes needed to obtain a quasi-uniform film (that's why thicknesses of about 200 μm are obtained).

3.3.3. GC900. Contrary to previous tests, the 3 series is rapidly sintered in a belt furnace (RS) at 1030°C (Table 6). Preliminary studies have shown that FS (1050°C—10 min) and RS (1030°C—10 min—heating ramp: 25 min) give similar results. However the GC900-1 test shows a dispersion in the permittivity values. The two other tests GC900-2 with a heating rate time enhanced to 60 min and GC900-3 with a hold time of 20 min instead of 10 min show that GC900-2 gives good and homogeneous results with less dispersion.

Table 6. GC900 results for a 1030°C—10 min RS (rapid sintering in a belt furnace).

(A/2C/T_3)	e (μm)	Density (g/cm^3)	ε_r	d_{33} (pC/N)
GC900-1	60–75	3.3–3.9	120–180	44–62
GC900-2	65–90	3.2–4	130–150	44–61
GC900-3	65–85	3.6–4.2	140–170	38–49

3.4. Comparison Between Bulk Ceramics and Thick Films Piezoelectric Coefficients

Thick films d_{33} values are near bulk materials ones (Table 7), certainly because of a very low radial coupling factor (k_p of around 0.04), so lateral clamping due to the alumina substrate has a negligible influence on d_{33}. The electric permittivity is lower: it's certainly due to the residual porosity of the active layer together with a smaller grain size.

The plane wave model provides approximate values of the electromechanical coefficients of the films (Table 8).

The materials values introduced in the model are:

– for the active material: $c_{33}^{E*} = 12.6$ N/m^2, $V_0^{E*} = 4410$ m/s, $Z_0^{E*} = 25.5$ Mrayls (calculated from standard IEEE on bulk PT),
– for the electrodes: $V_1 = 550$ m/s, $Z_1 = 1.4$ Mrayls, $l_1 = 27$ μm (values taking into account the important porosity of the electrodes),
– for the alumina substrate: $V_2 = 9165$ m/s, $Z_2 = 34.4$ Mrayls, $l_2 = 250$ μm. The density ρ_0 is

Table 7. Thick films and corresponding bulk ceramics characteristics (GC900).

GC900	Thick films (GC900-2)	Bulk ceramics
Density (g/cm^3)	3.2–4	6.45
ε_r	130–150	195
d_{33} (pC/N)	44–61	62

Table 8. Films coefficients evaluated from the plane wave model.

	Experimental measurements					Values derived from the model						
Ref	l_0 (μm)	d_{33} (pC/N)	fp (MHz)	ε_{33}^{T}	ε_{33}^{S}	x	ρ_0 (g/cm^3)	c_{33}^{E} (10^{10} N/m)	c_{33}^{D} (10^{10} N/m)	k_t	e_{33} (C/m^2)	h_{33} (10^9 V/m)
GC900-No. 1	55	61	10.180	147	98	0.55	3.47	2.22	2.43	0.30	1.35	1.56
GC900-No. 2	67	44	8.560	147	122	0.67	4.33	4.13	4.43	0.26	1.82	1.68
GC900-No. 3	85	49	8.380	127	101	0.57	3.70	2.64	2.83	0.26	1.29	1.45

approximatively the same as the experimental value, the factor k_t is more than half of the bulk one. However the model requires further improvements because results are very sensitive to the values used for electrodes and substrate.

4. Conclusion

Ca doped PT thick films have been successfully deposited on alumina substrates by screen-printing. Results are very satisfactory in comparison with the corresponding bulk material coefficients. A 50 pC/N (instead of 60 for bulk) d_{33} mean value is obtained which is in good agreement with a low planar coupling factor. The lower permittivities values (140 for films instead of 200) could be improved by investigations on ink elaboration, by addition of some fluxes for improved densification and by compression of the films before sintering. According to the potential applications of such materials, it could be interesting to study deposits on stainless steels and other substrates with lower acoustic impedance than alumina.

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