Journal of the European Ceramic Society 21 (2001) 1445–1449
www.elsevier.com/locate/jeurceramsoc

Preparation and electromechanical properties of PZT/PGO thick films on alumina substrate

Pascal Tran-Huu-Hue [a,*], Franck Levassort [a], François Vander Meulen [a], Janez Holc [b], Marija Kosec [b], Marc Lethiecq [a]

[a] LUSSI/GIP Ultrasons, EIVL, François Rabelais University, BP 3410, 41034 Blois cedex, France
[b] Josef Stefan Institute, Jamova 39, 1000 Ljubljana, Slovenia

Received 4 September 2000; received in revised form 7 November 2000; accepted 5 December 2000

Abstract

PZT thick films with lead germanate as low temperature sintering aid were prepared on alumina substrates. The thickness of films after sintering procedures reached 50 μm. Chemical compatibility and microstructure of layers was studied by EDS/SEM analysis. A fit between theoretical and experimental electrical impedance of several samples as a function of frequency is used to determine the elastic, dielectric and piezoelectric properties in thickness mode of the ceramic layers. Results for different poling fields (3 and 12 kV/mm) and sintering temperatures are obtained. Finally, the KLM equivalent circuit is used to obtain simulations of transducers integrating these thick films and their performance for medical imaging applications is evaluated.

Keywords: Films; Impedance; Piezoelectric properties; PZT; Tranducers

1. Introduction

For high frequency ultrasound medical imaging single crystals ($LiNbO_3$), traditional ceramics (PZT, PT) or 1-3 PZT fiber composites are traditionally used.[1] Lapping and machining are necessary to obtain a very low thickness (i.e. < 50 μm). The materials are subject to chipping and breaking and electromechanical performance can be deteriorated. An alternative solution is to use ferroelectric polymers (PVDF) or copolymers [P(VDF-TrFe)], but they possess relatively low thickness coupling factors (k_t < 30%). The addition of matching layers in order to increase sensitivity of these transducers is technically difficult, but is not necessary since these materials have low acoustical impedances (4~5 MRa). Thick films made with PZT ceramics by screen-printing,[2] or PZT-coating[3] have also been studied and characterised.

In this paper, characteristics in thickness mode of new PZT thick films (with lead germanate) deposited on alumina substrates by screen-printing are studied. A description of the fabrication process and the microstructure is given in the next section. A method based on a fitting process between experimental and theoretical impedance curves allowing dielectric and mechanical losses to be obtained is described. The results of the characterisation of six samples obtained with several sintering temperatures and poling fields on alumina substrate are discussed.

With a modified KLM scheme,[4] the properties of these materials are used as inputs to simulate single element medical transducers in two configurations to evaluate their performances.

2. Preparation of the samples

PZT 53/47 powder ($PbZr_{0.53}Ti_{0.47}$) was prepared by mixed oxide synthesis at 900°C for 1 h from PbO (litharge) 99.9% (Fluka), ZrO_2 99% (Tosoh) and TiO_2 99% (Fluka). Lead germanate with composition $Pb_5Ge_3O_{11}$ was added as sintering aid. Lead germanate (PGO) was also prepared by mixed oxide synthesis from PbO and GeO_2 99% (Ventron) powder. After synthesis, both powders were ball milled in acetone for 1 h and dried. Thick film paste for printing was prepared from PZT powder with addition of 2 wt.% of PGO by mixing

* Corresponding author. Tel.: +33-2-5455-8433; fax: +33-2-5455-8445.
E-mail address: tran@univ-tours.fr (P. Tran-Huu-Hue).

0955-2219/01/$ - see front matter
PII: S0955-2219(01)00038-3

with an organic vehicle on a roll mill.[5] Alumina substrates were prepared from alumina powder, Alcoa A-16, by sintering at 1700°C to near theoretical density. After the sintering process, the substrates were lapped and polished by diamond paste. Gold paste Remex 3243 was used as bottom electrode. The bottom gold electrode was screen printed on alumina substrate and sintered at temperature 950°C for 1 h. The PZT/PGO paste was printed, dried and presintered on gold electroded alumina substrates to the final thickness of ≈80 μm.

Finally, PZT layers were sintered at temperatures from 750 to 850°C up to 8 h. Samples were heated and cooled at 1°C min^{-1}. For electrical measurements, sputtered gold electrodes were deposited. Samples were poled at 150°C for 1 h in oil bath at 3 and 12 kV/mm. Fig. 1 is a photograph of the microstructure of a cross-sectioned sample.

3. Characterisation method of the PZT/PGO films on alumina substrate

Electrical, acoustical and electroacoustical parameters of thickness mode of six PZT/PGO samples on alumina substrate with different sintering temperatures and poling fields have been measured (Table 1).

The determination of the thickness mode parameters of the effective piezoelectric layer is delicate due to the alumina substrate. The method described by Cheeke et al.[6] is unfortunately not sufficiently precise and does not allow to obtain mechanical and dielectric losses. We have chosen a method close to the one described by Lukacs et al.[3] A fit between experimental curves and a theoretical expression of the electrical impedance as a function of frequency is performed.

The input electrical impedance around the thickness mode of a piezoelectric resonator on a substrate can be expressed by:[5]

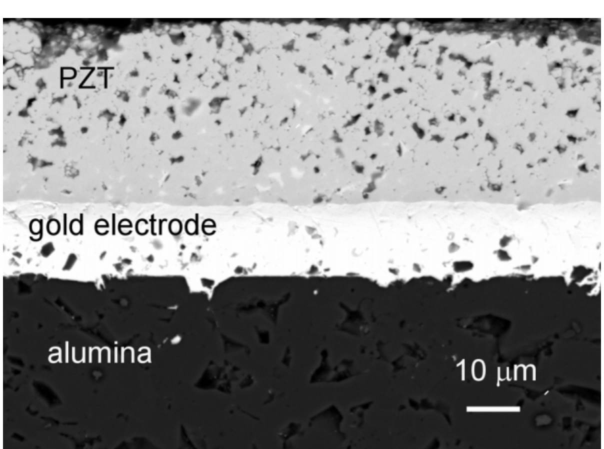

Fig. 1. SEM photograph of microstructure of cross-sectioned sample sintered at 800°C during 8 h.

Table 1
Geometric characteristics and parameters of the fabrication process of the six samples[a]

Sample	T_s (°C)/t (h)	E_p (kV mm^{-1})	Φ (mm)	e (μm)
1	750/8	12	3.2	49
2	750/8	3	3.19	49
3	800/8	12	3.08	43
4	800/8	3	3.12	47
5	850/8	12	3.20	49
6	850/8	3	3.10	50

[a] T_s/t, sintering temperature /duration; E_p poling field; Φ, diameter of the upper electrode; e, thickness of the film.

$$Z(\omega) = \frac{t}{\mathrm{i}\omega\varepsilon^{S}_{33r}\varepsilon_0 A} \times \left(1 - \frac{v_t^D k_t^2}{\omega t} \frac{2Z_c \tan\left(\frac{\omega t}{2v_t^D}\right) + Z_b \tan\left(\frac{\omega t_b}{2v_b}\right)}{Z_c + Z_b \tan\left(\frac{\omega t_b}{2v_b}\right)\tan\left(\frac{\omega t}{2v_t^D}\right)}^{-1}\right) \tag{1}$$

where ω is the angular frequency (rad s^{-1}), ε_0 the dielectric constant of vacuum (F m^{-1}), A the electrode area (m^2). The constants of the piezoelectric thick film are ε^S_{33r} the relative dielectric constant at constant strain, t the thickness (m), $k_t = \frac{e_{33}}{\sqrt{c^D_{33}\varepsilon^S_{33}}}$ the electromechanical coupling factor in thickness mode, $v_t^D = \sqrt{\frac{c^D_{33}}{\rho}}$ the longitudinal wave velocity (m s^{-1}), Z_c the acoustical impedance (Ra), c^D_{33} the elastic stiffness coefficient at constant electrical displacement (N m^{-2}) and ε_{33} the piezoelectric coefficient cm^{-2}. The constants of the alumina substrate are: t_b the thickness (m), v_b the longitudinal wave velocity (m s^{-1}), and Z_b the acoustical impedance (Ra).

Here, mechanical (δ_m) and dielectric (δ_e) losses are introduced, and complex elastic coefficient ($C^{E^*}_{33}$) and dielectric constant ($\varepsilon^{S^*}_{33r}$) are used in Eq. (1):[4]

$$C^{E^*}_{33} = C^{E}_{33}(1 + i\delta_m) \qquad \varepsilon^{S^*}_{33r} = \varepsilon^{S}_{33r}(1 - i\delta_e) \tag{2}$$

Using the geometrical characteristics and the densities of the different elements, a fit of the experimental electrical impedance with Eq. (1) allows to determine all other parameters.

To reduce the number of unknown variables, the substrate parameters appearing in Eq. (1) are first measured. Attenuation measurements (to deduce mechanical losses) were performed by the transmission method in water using wideband transducers of centre frequency 10 MHz. The velocity is determined from the measurement of the time of flight by intercorrelation between the reference signal (in water) and the signal transmitted through the sample.

The results obtained show that the attenuation curve between 8 and 12 MHz is quasi-linear. By extrapolation, we have assumed that this variation is valid from 1 to 70 MHz, corresponding to the frequency range of the electrical impedance measurements. All the characteristics of the alumina substrate are given in Table 2.

4. Results and discussion

The experimental set-up is composed of a HP4195 network analyser and its impedance test kit with a spring clip-fixture where all the upper faces of the sample are placed under free resonator piezoelectric conditions and electrical contacts are kept clean.

Experimental and theoretical complex electrical impedances of sample 3 are shown in Fig. 2 between 1 and 70 MHz. A very good agreement is observed between the two curves.

Fig. 3 represents the same curves in a narrow frequency range (between 25 and 31 MHz), so that the experimental and theoretical resonance peaks are clearly observed. The results of the characterisation of the six samples are given in Table 3.

In these samples, the electrode thicknesses are not negligible in comparison to the thickness of the piezoelectric layer. In the characterisation method used here, the electrodes are not taken into account, so the parameters that we obtain corresponds to effective materials composed of the electrodes and the piezoelectric layer.

The most significant differences between the sample parameters are observed on the thickness coupling factors (3–42%) and the dielectric constant at constant strain (365–490). The number of samples characterised is too low to give a definitive conclusion concerning the

Table 2
Properties of the alumina substrate used for the six samples[a]

Sample	v_l (m s^{-1})	e (mm)	α (dB/mm/MHz)	ρ (kg m^{-3})
Alumina	10 500	3.34	0.006	3900

[a] v_l, longitudinal wave velocity; e, thickness of the substrate; α, attenuation in the substrate; ρ, density.

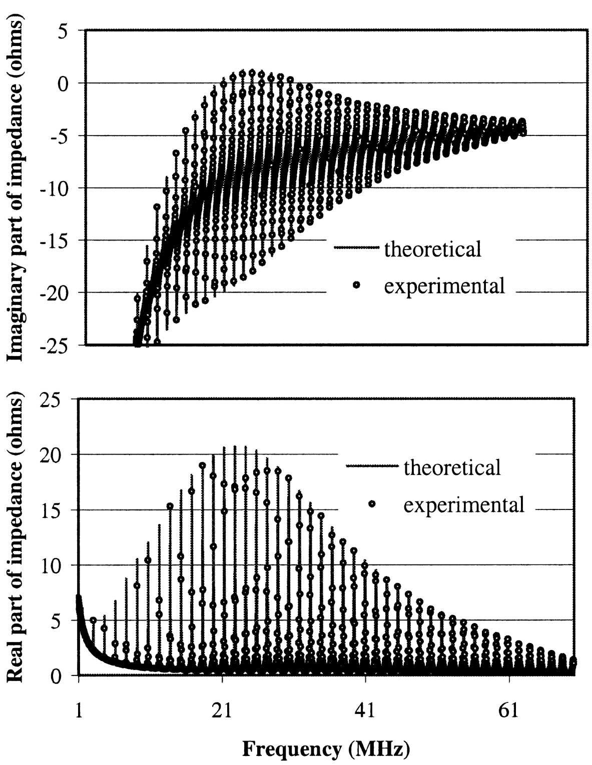

Fig. 2. Theoretical and experimental complex electrical impedance of sample 3 as a function of frequency in a large range of frequencies (1–70 MHz).

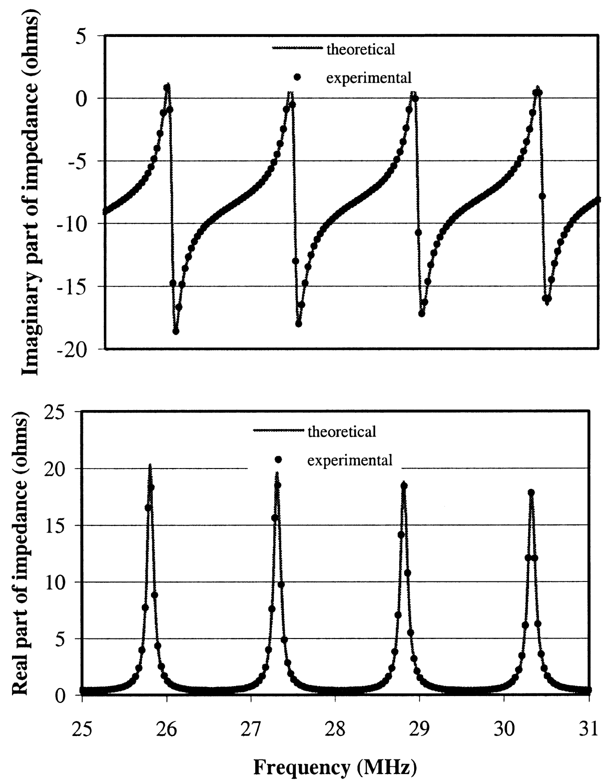

Fig. 3. Theoretical and experimental complex electrical impedance of sample 3 as a function of frequency between 25 and 31 MHz.

Table 3
Electromechanical properties of the samples[a]

Sample	k_t (%)	ε^S_{33r}	v_l (m s^{-1})	f_a (MHz)	δ_m (%)	δ_e (%)
1	25	365	4200	43	3	3
2	15	400	4200	43	3	3
3	42	365	4200	49	3	3
4	7	420	4200	45	3	3
5	Not poled	490	Not poled	Not poled	Not poled	Not poled
6	3	490	4200	42	3	3

[a] k_t, thickness mode coupling factor; $\varepsilon^S_{33}/\varepsilon_0$, relative dielectric constant at constant strain; v_l, longitudinal wave velocity; f_a, antiresonance frequency; δ_m, mechanical losses; δ_e, dielectric losses.

optimum poling conditions, in particular sample 5 has not been correctly poled, probably due to a short-circuit.

The thickness coupling factor value of 42% for sample 2 is a very promising result in comparison with those of polymers and copolymers (i.e. $k_t < 30\%$) or PZT-coating[3] (i.e. $k_t < 25\%$). The dielectric constant is also higher (~400) than that of copolymers (~6) and PZT sol-gel composites (~220).[3]

To evaluate the performance of single-element transducers integrating the PZT/PGO thick films (values of sample 3), two simulations with a modified KLM scheme including mechanical and dielectric losses have been performed. Fig. 4 represents the electroacoustic impulse response of a transducer on alumina backing, assuming that its thickness is infinite, and with no matching layer. The active area of the transducer is that of sample 3. The electroacoustic impulse response of a transducer in a similar configuration but with a quarter-wavelength matching layer is given in Fig. 5. Table 4 summarises acoustical impedances and thicknesses of each element of the simulated transducers.

These two pulse–echo electroacoustic responses give, respectively, axial resolutions at −6 dB of 52.5 μm and 85.5 μm; −6 dB bandwidths of 108 and 69% for a centre frequency of 22.2 MHz. The centre frequency of the transducers corresponds to a $\lambda/4$ resonance due to the higher acoustic impedance of the backing compared to that of the piezoelectric material.

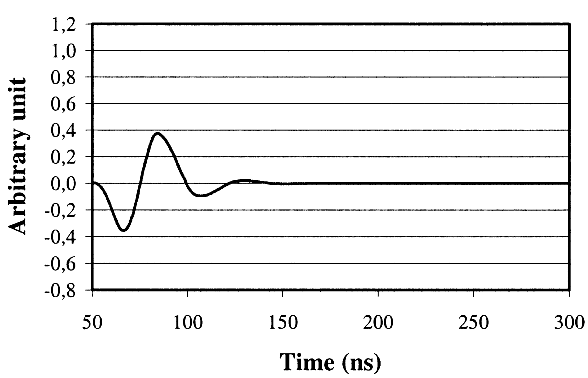

Fig. 4. Electroacoustic impulse response of the transducer with no matching layer.

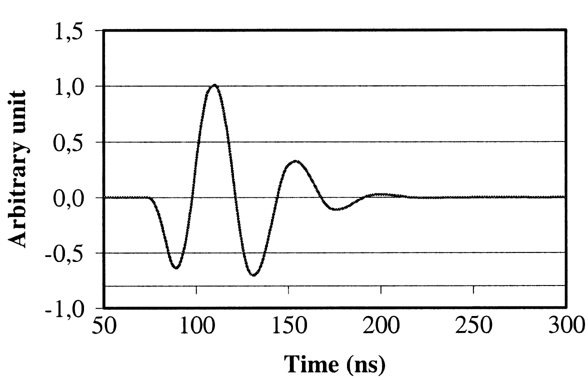

Fig. 5. Electroacoustic impulse response of the transducer with one matching layer.

Table 4
Properties of the different transducer elements for the simulations[a]

Transducer element	Z (MRa)	e (μm)
Piezoelectric (sample 3)	30.2	43
Backing (alumina)	41.5	Infinite
Matching layer	4	28

[a] Z, acoustical impedance of the element; e, thickness of the element.

5. Conclusion

Several samples made of a new piezoelectric material deposited on alumina substrates by screen-printing have been produced and characterised. The layer obtained has a thickness around 45 μm. To reduce the number of parameters for the fit between the experimental electrical impedance of samples and the theoretical curve, the acoustic properties of the alumina substrate have been measured independently.

Results, in particular the coupling coefficient (42%) and dielectric constant (~400), are promising and allow to conclude that the use of these materials for high frequency ultrasound applications is possible. However, the alumina substrate is not an optimal choice for backing since its attenuation is very low, which imposes a very large thickness to avoid backwall echoes. Moreover, its acoustic impedance is higher than that of the piezoelectric layer, and consequently the centre frequency of the transducer is divided by approximately two and the sensitivity is reduced. A substrate compatible with the fabrication process and with adequat acoustical properties (i.e. higher attenuation and acoustical impedance <20 MRa) must be identified in order to obtain higher transducer performance.

Acknowledgements

This work was funded by the French Research Ministry in the on-going EUREKA project PIMET (EU1664).

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