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Processing of High Performance Lead Lanthanum Zirconate Titanate Thick Films

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Abstract

The processing and ferroelectric properties of lead lanthanum zirconate titanate (PLZT) thick films on Pt-coated Al_2O_3 *substrate were studied. The most critical processing issue is to prevent lead losses during heat treatment. Maintaining a high PbO vapour concentration during heat treatment of the layers maintains a liquid phase that enables densification also in constrained conditions, possibly because of relaxation of the shear stress originating from constrained sintering. Reaction of PbO-rich liquid phase at the platinum/alumina interface results in β-alumina crystals that deteriorate the contact between the platinum electrode and the substrate. Instead of platinum on* Al_2O_3*, a new* Al_2O_3*/PLZT/Pt structure was introduced taking advantage of the excellent mechanical stability of the* Al_2O_3*/PLZT and Pt/PLZT interfaces. PLZT thick films with ferroelectric properties equal to or better than those of hot pressed samples were obtained. Such a sintering and electrode strategy can be applied in processing of other lead-based thick films. © 1999 Elsevier Science Limited. All rights reserved*

Keywords: thick films, sintering, interfaces, ferroelectric properties, PLZT.

1 Introduction

Ferroelectric thin films of thickness commonly below 1 μm have been extensively investigated due to their potential applications in microelectronics and micromechanics. Much less attention has been paid to processing of thicker films, although quite a number of applications require films of several microns to several tens of microns. Whereas ferroelectric thin film methods have their specific features, ferroelectric thick film processing is closer to that of the bulk ceramics, and includes powder synthesis, powder processing, coating and sintering. Coating can be achieved by screen printing, a well developed processing step in thick film technology.

Research on ferroelectric thick films is essentially limited to lead zirconate titanate-based materials, mostly for specific applications. Examples are pyroelectric sensors,[1,2] gravimetric sensors,[3] micropumps,[4] pressure sensors,[5] and surface acoustic wave (SAW) devices.[6] Properties obtained are poorer compared to the bulk ceramics due to the addition of low temperature sintering aids and/or high porosity.

Recently it was shown that ferroelectric ceramics can be used for high speed electrophoretic printing, utilising their memory effect.[7] Rhombohedral lead lanthanum zirconate titanate (PLZT) is a candidate for this application because of its rectangular hysteresis loop, of a high remanent polarisation (Pr) and a low coercive field (Ec).

This application also requires a highly dense structure with negligible defects that can sustain a number of rewriting cycles. According to thickness requirements, thick film structures may be a solution. This paper reports critical aspects of processing of dense PLZT layers on electroded alumina substrates. Coating was accomplished by screen printing. Particular attention was paid to densification of constrained layers, PLZT/electrode/ substrate interactions and the ferroelectric properties of sintered layers.

2 Experimental

PLZT 8/65/35 powders were prepared by mixed oxide synthesis. The composition was based on a formula predicting A-site vacancies, namely $Pb_{1\text{-}3x/2}La_xZr_{0\cdot65}Ti_{0\cdot35}O_3 + y$ mole% excess PbO with $x = 8$ and $y = 1$ (denoted as PLZT 1 Pb) and $y = 6$ (denoted as PLZT 6 Pb).

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PbO (litharge) 99·9% (Fluka), 99·0% ZrO_2 (Tosoh), 99·0 TiO_2 (Fluka) and $La(OH)_3$ were weighed in the required quantities. $La(OH)_3$ was prepared from 99·99% La_2O_3 (Alfa) by equilibrating it in humid atmosphere for 3 days. The stoichiometry of the hydroxide was checked by thermogravimetry. Starting chemicals were mixed together in acetone in a zirconia ball-mill for 2 h. After drying the mixture was calcined at 900°C for 2 h, re-milled and calcined again. After the second calcination, the powder was milled for 1 h and dried. A nonagglomerated fine particle size powder of a mean particle size of 0·8 μm as measured by granulometry (Cilas) and checked by SEM (Jeol JSM5000) was obtained. According to XRD analysis (Philips PW 1710) PLZT solid solution formation was completed during synthesis.

Thick film ink was prepared from the synthesised powder and an organic vehicle (α-terpineol, butyl carbitol, and ethyl cellulose) by mixing them in a roll-mill.Alumina substrates were prepared by slip casting of alumina powder, Alcoa A-16, and sintering at a temperature of 1700°C for 4 h to closed porosity. After the sintering process the substrates were lapped and polished with diamond paste. The dimensions of the substrates were $30\times30\times2{\cdot}5$ mm. A trace of glass phase was detected on the polished surface. According to SEM/EDS analysis a second phase containing Ca, Mg, Si and Na in addition to Al_2O_3 was formed due to the presence of impurities in the alumina powder.

Demetron platinum paste without any glassy phase, type 410, was used as the bottom electrode. The electrode was screen printed on the alumina substrate. After drying at 150°C it was sintered at 1400°C for 2 h. The pulling force needed for delamination of the metallic layer from the alumina substrate was measured. Two rods of aluminium were glued on each side of the metallised substrate with epoxy glue. The pulling strength was determined on an Instron 1362 testing machine. Good adhesion of platinum electrodes to the alumina substrate was found. The pulling strength on the test samples was more than 2000 N cm^{-2}. This was the limiting strength of the alumina rod/epoxy bond.

After electrode deposition, the PLZT layer was screen printed up to 85 μm thick. One printing step resulted in an $\sim$10 μm thick layer. Films were additionally densified by isostatic pressing at 200 MPa. Pressing improves the quality of thick PZT based films.[2] After that the films were presintered at 600°C, 1 h to remove organic.

PLZT layers were sintered at 1100°C for 2 and 8 h in a closed alumina crucible. Atmosphere powder was put close to the PLZT layer to provide a PbO rich atmosphere. Two types of atmosphere powder were used, $PbZrO_3 + 2$ w/o ZrO_2, and $PbZrO_3 + 2$ w/o PbO. Samples were heated at 2°C min^{-1} and cooled down at 1°C min^{-1}. To check the sintering behaviour of PLZT, the powder was pressed into pellets of 6 mm in diameter and 4 mm height. Pellets were heated at 5°C min^{-1} up to 1300°C in a heating microscope. Shrinkage versus temperature was obtained from photographs. SEM analyses were performed to analyse the surface of the layers as well as polished and thermally etched cross sections. EDS analysis was applied to identify the chemical composition of various reaction products.

For electrical measurements sputtered gold electrodes were deposited. The values of remanent polarisation and coercive field were determined from ferroelectric hysteresis curves measured by a Sawyer–Tower bridge and registered by a Nicolet Pro 30 digital oscilloscope. The real and the imaginary part of the complex dielectric constant was measured by an HP 4284 A Precision LCR Meter at 1 kHz.

3 Results and Discussion

3.1 Sintering

Figure 1 presents the shrinkage versus temperature curves for PLZT pellets containing 1 and 6 mole% excess PbO. Densification of the former takes place at temperatures above 1200°C. However, some shrinkage is observed at 900°C and indicates a liquid phase locally present, causing limited rearrangement.[8] Samples containing 6 mole% excess PbO start densifying soon after 800°C, when liquid phase appears according to the phase diagram for PbO–TiO_2–ZrO_2.[9] Rapid densification is observed above 1000°C. The results are in agreement with published data showing that the densification of PLZT takes place at a lower temperature in proportion to the amount of excess PbO and the corresponding increase in liquid phase.[10,11] However, it should be

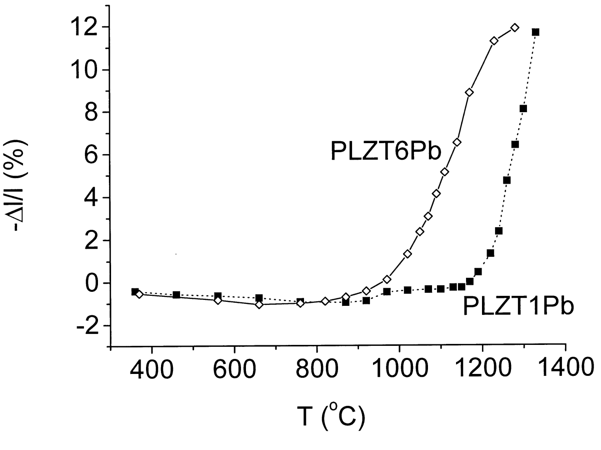


Fig. 1. Shrinkage versus temperature of PLZT pellets.

pointed out that our compositions are based on the assumption of the A-site vacancy compensation mechanism and not on the commonly assumed B-site compensation. The PLZT 6 Pb sample (A-site compensation) corresponds to the stoichiometric composition represented by the formula $Pb_{1-x}La_x$-$(Zr_{0.65}Ti_{0.35})_{1-x/4}O_3$ for the B-site compensation.

PLZT 1 Pb that contains 1 mole% excess PbO according to A-site vacancy compensation is strongly substoichiometric with respect to B-site compensation. The observed small low temperature densification of PLZT 1 Pb supports the prevailing A-site compensation mechanism, at least at the synthesis temperature of 900°C. Thick film structures were sintered at 1100°C for 2 and 8 h in a closed alumina crucible containing atmosphere powders with low and high PbO activity, namely $PbZrO_3$–ZrO_2 and $PbZrO_3$–PbO. Note that activity of PbO over $PbZrO_3$–ZrO_2 is higher than over PLZT-ZT, therefore no decomposition of PLZT is expected.

Thick films sintered in an atmosphere with low PbO activity are porous as shown in Fig. 2(a) independently of the excess of PbO in the starting composition.

Thick films sintered in the atmosphere provided by $PbZrO_3$–PbO are dense, already after two hours of sintering independently of the amount of PbO present in the starting powder [Fig. 2(b)–(d)]. Sintering of PLZT with excess PbO occurs in the presence of liquid phase. Rearrangement of particles due to capillary forces is the dominant mechanism of densification, particularly during sintering at lower temperatures.[11] Sintering of thick films takes place under constrained conditions. During constrained sintering a tensile stress would develop in the plane of the film producing a shear stress.[12] In the presence of liquid phase it could be relaxed by shear strain through the accommodation of particles, leading to further densification. To obtain a high density, liquid phase, though only small amounts as in the case of PLZT 1 Pb, has to be present in the film during the whole sintering stage. This is assured in an atmosphere with a high PbO partial pressure, maintained by the atmosphere powder with high PbO activity, namely $PbZrO_3$–PbO.

Sintering of PLZT films with excess PbO in the atmosphere with a low PbO partial pressure results in low density, as shown in Fig. 2(a). The top surface of the film indicates a dense region separated by large pores. After the initial rearrangement, regions of higher density are formed, producing pores in between. In a nonconstrained film, when

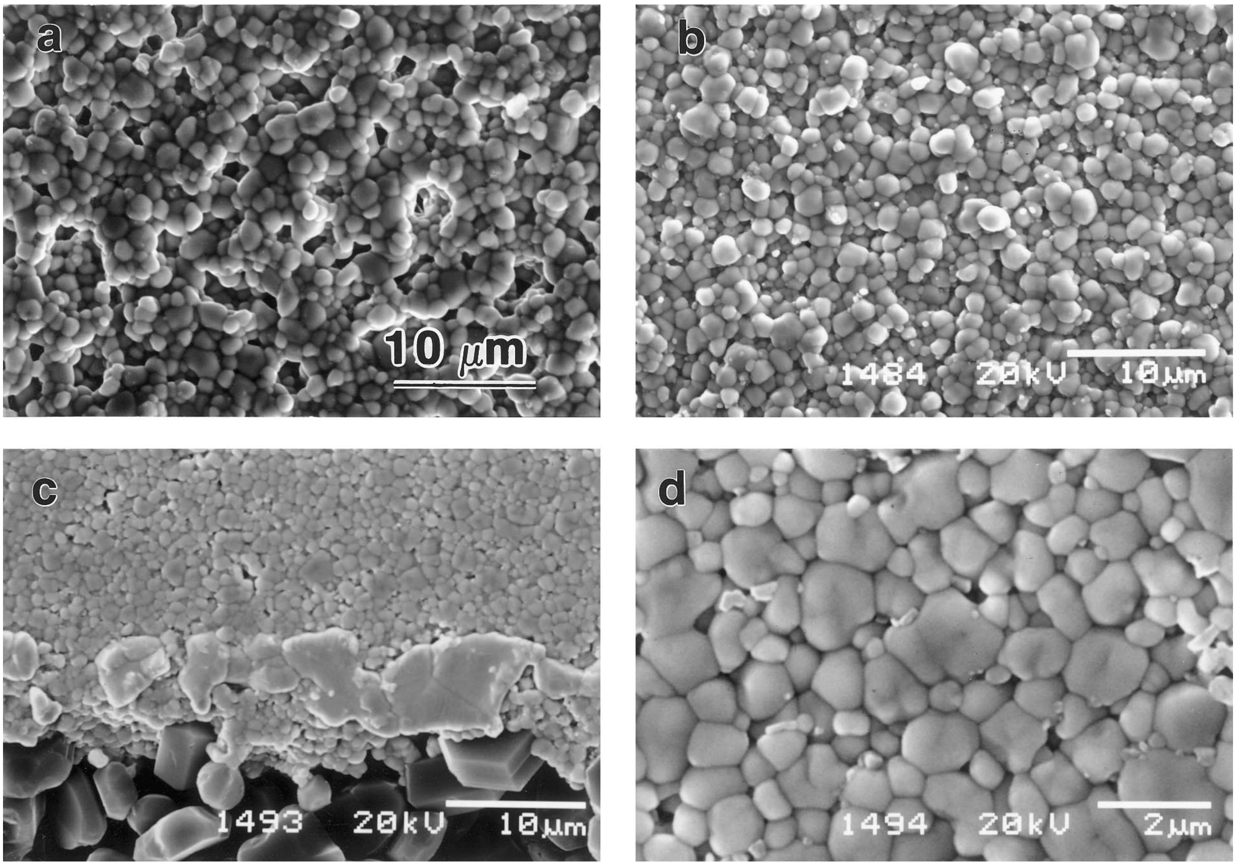


Fig. 2. SEM micrographs of PLZT thick films: (a) PLZT 6 Pb 1100°C, 8 h, $PbZrO_3$–ZrO_2, surface; (b) PLZT 1 Pb 1100°C, 2 h, $PbZrO_3$–PbO, surface; (c) PLZT 1 Pb 1100°C, 2 h, $PbZrO_3$–PbO, cross-section; (d) PLZT 1 Pb 1100°C, 2 h, $PbZrO_3$–PbO, microstructure of PLZT layer.

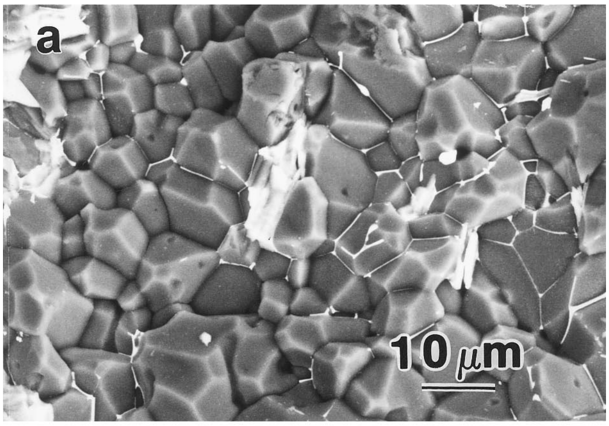
the liquid phase disappears, densification would continue by solid state sintering. Constrained conditions limit this process.[13]

3.2 Interface reactions

Unfortunately the presence of a PbO rich liquid phase in PLZT that promotes densification has a detrimental effect on the stability of the Pt/Al_2O_3 interface. The adhesion between Pt and PLZT is good. We have never found any delamination at this interface. However, the PLZT thick film structure easily delaminates at the platinum-alumina interface. The pulling strength of films sintered at 1100°C 8 h is less than $10\,N\,cm^{-3}$. SEM pictures of the platinum and alumina surface in contact during sintering of PLZT 6 Pb for 8 h at 1100°C are presented in Fig. 3. The alumina surface [Fig. 3(a)] contains a solidified liquid phase between the Al_2O_3 grains.

The platinum surface is covered with crystals that according to XRD have the structure of β-alumina (PbO.6 Al_2O_3). EDS analysis revealed traces of additional elements Ca, Mg, Ti and La. Well faceted crystals sticking to Pt, support a flux growing mechanism with nucleation on the Pt surface. It is proposed that the PbO rich liquid containing Ti and La passes through pores in the Pt to Al_2O_3 surface and reacts with alumina. After reaction and saturation with Al_2O_3, β-alumina crystals start to grow and separate Pt and alumina.[14] Reaction between PLZT and alumina itself gives the same product, namely β-alumina; however it grows inside the alumina giving a dense, mechanically stable interface. Taking into account the mechanically strong interface of Pt-PLZT and PLZT-Al_2O_3, we designed a new thick film structure as shown in Fig. 4.[15] The alumina surface is covered with PLZT, sintered, and covered with Pt. After sintering of the Pt layer at 1100°C, an active PLZT layer is screen printed and sintered as already described (Fig. 5).

There are several advantages of a new structure. In addition to excellent mechanical stability of the interfaces, platinum loses its function as a barrier layer due to the equal chemical potential of PLZT on its top and bottom. Therefore its thickness can be decreased, and it does not need to be sintered at high temperature since there is no need for it to be highly dense. It is worthwhile mentioning that because of the lack of transport through Pt,



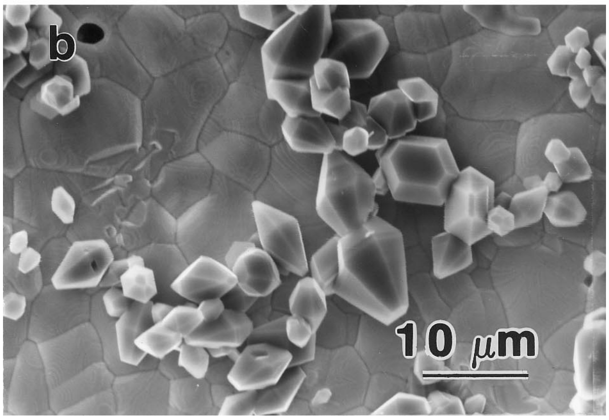


Fig. 3. SEM micrographs of PLZT 6 Pb, 1100°C, 8 h, interface Al_2O_3/Pt: (a) Al_2O_3 surface; (b) Pt surface.

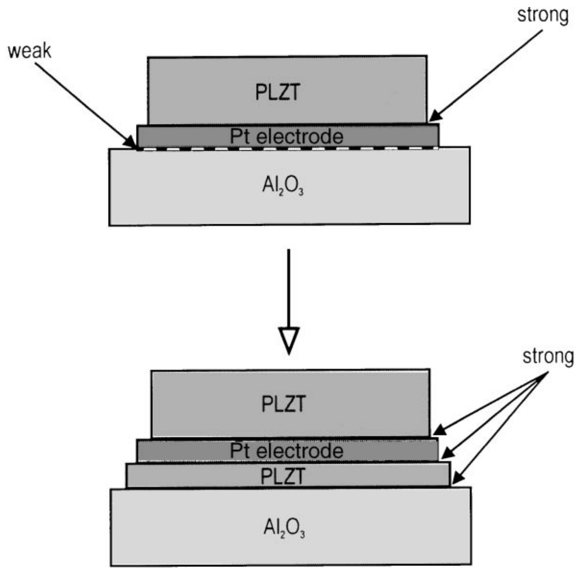


Fig. 4. New thick film structure (schematically).

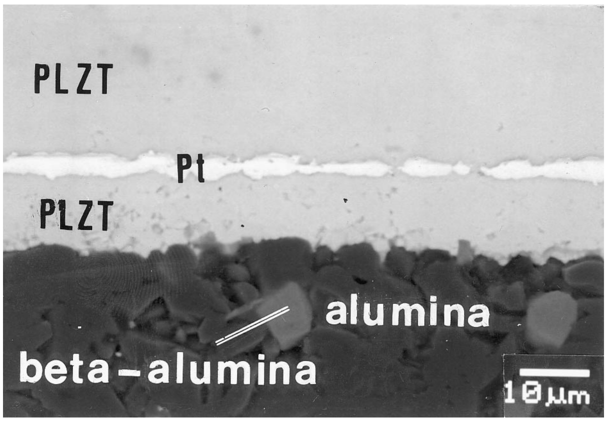


Fig. 5. SEM micrograph of Al_2O_3/PLZT/Pt/PLZT structure (PLZT 6 Pb, 1100°C, 8 h).

Table 1. Room temperature remanent polarisation Pr, coercive field Ec, the real (ε') and imaginary (ε'') part of the dielectric constant at 1 kHz for PLZT thick films on Pt or Pt/PLZT electrode structure and alumina substrate

Thick film (thickness 40–45 μm)	*Pr (μC cm^{-2})*	*Ec (kV cm^{-1})*	ε'	ε''
PLZT 6 Pb 1100°C/8 h/Pt	31·1	3·91	6534	265
PLZT 6 Pb 1100°C/2 h/Pt	29·5	3·61	6260	420
PLZT 6 Pb 1100°C/8 h/Pt/PLZT	30·2	7·9	4290	130
PLZT 1 Pb 1100°C/8 h/Pt/PLZT	23·1	6·96	3623	209
PLZT 1 Pb 1100°C/2 h/Pt/PLZT	19·0	6·58	2895	182
Bulk ceramics:				
HP Ref. 16	30	3·6	3400	102
HP Ref. 17	20	3	4692	235
Normal sintering:				
Ref. 18	19	7	2860	160

the chemical composition of PLZT layer is well preserved.

3.3 Electrical properties

Table 1 presents some electrical data on the PLZT thick layer.

Data from Refs. 16 and 17 are for hot pressed samples, whereas data from Ref. 18 are for conventionally sintered ceramics. As confirmed in Table 1, PLZT thick films on alumina substrates with Pr values equal to or better than bulk ceramics and low Ec are regularly processed. Good ferroelectric properties are ascribed to the high density of the films. According to thermal expansion coefficients of Al_2O_3, Pt and PLZT (which is assumed to be not very much different from rhombohedral PZT), the films are under compressive stress that favours a high Pr value and a low Ec.[17] PLZT thick films additionally show better fatigue than conventionally sintered bulk ceramics[19] and have a high d_{33} value.[20]

4 Conclusions

Highly dense thick PLZT films of approximately 40 μm with superior ferroelectric properties were prepared on platinum coated alumina. Maintaining a high PbO vapour pressure during heat treatment of the layers maintains a liquid phase that enables densification also in constrained conditions, possibly because of relaxation of shear stress originating from constrained sintering.

Reaction of PbO rich liquid on the Pt/Al_2O_3 interface deteriorates the mechanical contact between Al_2O_3 and Pt. To avoid this, a new electrode structure consisting of Al_2O_3/PLZT/Pt was introduced, taking advantage of the excellent stability of Al_2O_3/PLZT and PLZT/Pt interfaces. Such films show high remanent polarisation comparable to hot-pressed bulk ceramics, and a low coercive field. These sintering and electrode strategies can be used in processing of other lead based thick films.

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