Available online at www.sciencedirect.com
ScienceDirect
Journal of the European Ceramic Society 27 (2007) 4359–4362
www.elsevier.com/locate/jeurceramsoc

Screen printed PLZT thick films prepared from nanopowders

B.D. Stojanovic [a,*], V. Mitic [b], V. Pejovic [a], M.M. Vijatovic [a], M.A. Zaghete [c]

[a] *Centre for Multidisciplinary Studies of the Belgrade University, Serbia and Montenegro*
[b] *Faculty of Electronic Engineering, University of Nis, Serbia and Montenegro*
[c] *Instituto de Quimica-UNESP, Araraquara, S.P., Brazil*

Available online 9 April 2007

Abstract

The gap between the bulk materials and thin films can be filled with thick films suitably designed and appropriate processed. Thick films of complex system like lead–lanthanum–zirconium titanate (PLZT) is difficult to produce by simple solid-state reaction keeping compositional homogeneity and optimal grain size distribution. In the present work, PLZT thick films were fabricated by screen-printing technique from nanosized powders obtained through soft chemistry by polymeric precursor method. Thick film paste was obtained by mixing PLZT fine powders and organic vehicle. The upper and bottom electrodes based on Ag–Pd and functional component based on PLZT were screen-printed on alumina substrate and after that annealed in air atmosphere. The powder morphology, microstructure, dielectric and ferroelectric properties of 9.5/65/35 PLZT thick films were analysed.

Keywords: Films; Electron microscopy; Dielectric properties; Ferroelectric properties; PLZT

1. Introduction

The difficulty in the preparation of thin films in various thickness ranges is the primary reason for their availability. As the film thickness increases, the problem to prepare thicker films is well recognized. The gap between the bulk materials and thin films can be filled with thick films suitably designed and appropriate processed.[1] Unlike thin films, the number of processes capable for producing high quality thick films is rather limited.[2–4] It was shown that films thicker than 2–3 μm fabricated by dip-coating, spin-coating, electrophoresis, CSD precursors and chemical vapor deposition techniques had a strong tendency to undergo cracking, de-bonding from substrates, increasing the roughness.[4,6] Otherwise, the deposition of thick film by screen-printing is a relatively simple and convenient method to produce thick layers with thickness up to 100 μm. This process is useful to accommodate the demands of miniaturization, circuit complexity, multilayer assembles, or high frequencies demands.[5–8]

The circuits defined by screen-printing are fired typically at 850 °C to fuse the films to the substrates. This temperature is higher than the one required for thin films, thus increasing the possibility of interaction with either electrodes or substrates, consequently leading to a possible degradation. Adhesion between support and film and similar temperature expansion coefficients of the thick films and substrate are requested. Recently, low-melting glasses were used to isolate the top layer conductor from the rest of the circuit below. Due to undesirable interaction between the glass phase and the overlying conductor, crystallizable glasses with low dielectric permittivity have tendency to be formed.[9,10,17]

In general, the sub-micron powders are widely used to prepare thick films. Reliable ceramic powders can be obtained by various synthesis techniques including conventional oxide procedure, soft chemistry, physicochemical or physical processes. In our previous work, we have been reported the preparation of barium titanate thick films from powders by mechanically assisted synthesis.[11,12] Preparation of thick films based on ceramic powder of complex system like lead–lanthanum–zirconium titanate (PLZT) is more difficult to produce through simple solid-state reaction keeping compositional homogeneity and optimal grain size distribution. Due to complete miscibility between lead zirconate and lead titanate, and the substantial solubility (up to 40 atomic per cent at the high $PbTiO_3$ end) of lanthanum oxide in the system, it is possible to custom-make various combinations of chemical compositions to get specific desirable properties.

* Corresponding author.
E-mail address: bilijana@ibiss.bg.ac.yu (B.D. Stojanovic).

0955-2219/$ – see front matter © 2007 Elsevier Ltd. All rights reserved.
doi:10.1016/j.jeurceramsoc.2007.02.170

Although PLZT ceramics are constituted of a wide variety of compositions, from those suitable for piezoelectric applications to those specifically designed for pyroelectric devices, they are widely known for their electrooptic properties.

Soft chemistry has become popular for producing ceramic materials with improved compositional homogeneity and with lower sintering temperature. Polymeric precursor process employs complexion of cations in an organic media using low cost precursors and results in homogeneous ion distribution at molecular level.[12–14] Due to formation of polyester resin during the synthesis, no segregation of cations was observed during thermal decomposition of organic material. This process presents many advantages, such a possibility to work in aqueous solutions with high stoichiometry control. It is a low-temperature process and a cost-effective method due to inexpensive precursors and equipments.

In the present work PLZT thick films were fabricated by screen-printing technique from nanosized powders obtained from polymeric precursor by Pechini process. The aim of our work is to show the benefit of the named process not only in ceramic or thin film technology then also for thick film preparation of complex compound like is PLZT. Thick film paste was obtained by mixing PLZT fine powders and organic vehicle. The upper and bottom electrodes based on Ag–Pd and functional component based on PLZT were screen-printed on alumina substrate and after that annealed in air atmosphere. The morphology of powders, specific surface area, microstructure and electrical properties were carried out.

2. Experimental procedure

PLZT nanosized powders were prepared according to chemical formula $Pb_{0.905}La_{0.095}(Zr_{0.65}Ti_{0.35})_{0.976}O_3 + 3.5$ wt% PbO. The polymeric precursor process starting from the organometallic complex was employed. An excess of 3.5 wt% of PbO was added to the initial solutions to compensate the loss of PbO during firing processes. The details about procedure is presented in Ref. 13. It was shown by XRD results that the obtained powders indicated to the formation of cubic perovskite PLZT fase with small amount of PbO, less then 1%.[14]

The paste was prepared from the suspension of organic material (resin, organic solvent and additives to improve rheological behavior of paste) and calcinated PLZT powders, in relation 30:70. To get better adhesion between paste and substrate it was added a low temperature melting glass in powder form. The viscosity of the prepared paste was adjusted by viscosimeter in the range $0.6–1.1 \times 10^2$ m Pa s for shear rate $10\ s^{-1}$. The details about preparation of paste are presented in Refs. [15,16].

Alumina substrates were used as a commercial product (Alcoa). The electrode materials were specially produced (IRITEL dd.) for the screen-printing technique starting from the silver/palladium mixture (Ag–Pd 70/30). The bottom electrode was deposited on the Al_2O_3 support, in the middle was screen-printed layer of PLZT and on the top was deposited the upper electrode, sintered all together at 800 °C during 1 h in air flow atmosphere. The obtained films possessed a thickness ranging from about 25 to 75 μm, depending on the number of layers.

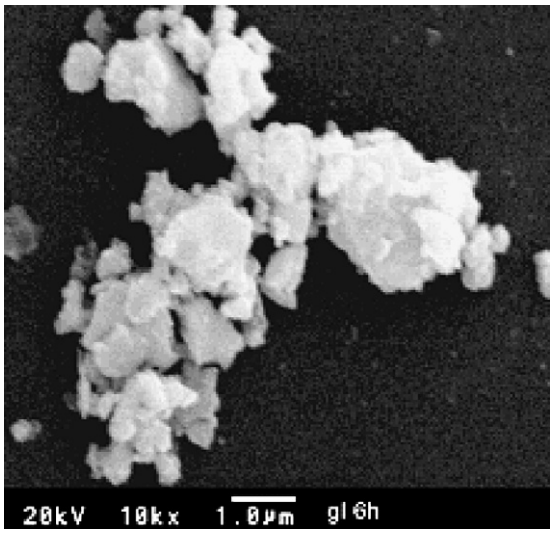

Fig. 1. SEM micrograph of PLZT powder calcinated at 700 °C/2 h.

The particle size analysis of as-prepared PLZT powders has shown that the obtained particles were less then 20 nm. The rather strong agglomerates were mainly destroyed by multi-step ultrasonic treatment of PLZT powders dissolved in kerosene. Scanning electron microscope-SEM (TOPCON SM 300) coupled with energy disperse spectrometer (EDX, Princeton Gamma-Tech) and transmission electron microscope (TEM, Model Philips CM200) were used to analyse powder morphology, PLZT functional phase microstructure and film thickness.

The electrical measurements, capacitance and dielectric losses are performed using a HP 4291A coupled with a furnace. The dielectric permittivity and Curie temperature were determined on the 3 layers for thick film samples with. The hysteresis loop was obtained using ACR 100 m.

3. Results and discussion

PLZT powders prepared by polymeric precursor method show after calcination good crystallinity and no evident presence of secondary phases. The morphology of powders and particle size is possible to observe in the Figs. 1 and 2, obtained by SEM and TEM analysis. The fact that the powders show strong agglomeration is well-known problem of reactive pow-

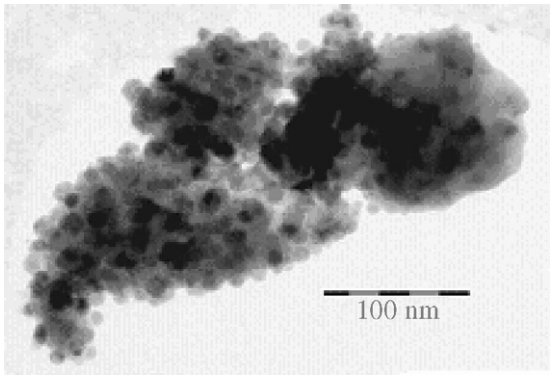

Fig. 2. TEM micrograph of 9.5/65/35 PLZT powder calcinated at 700 °C/2 h.

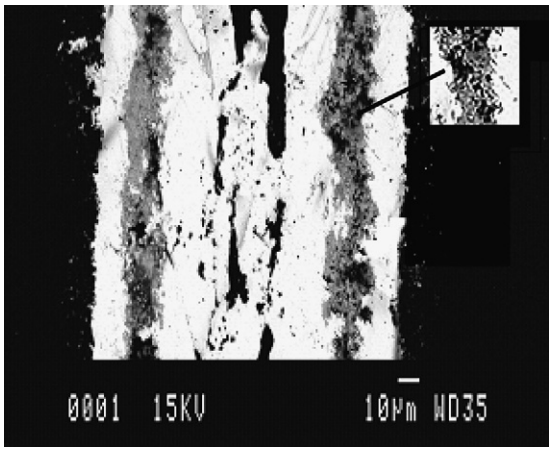

Fig. 3. Transversal section of PLZT thick film. In inset is presented grain size of 9.5/65/35 PLZT thick film.

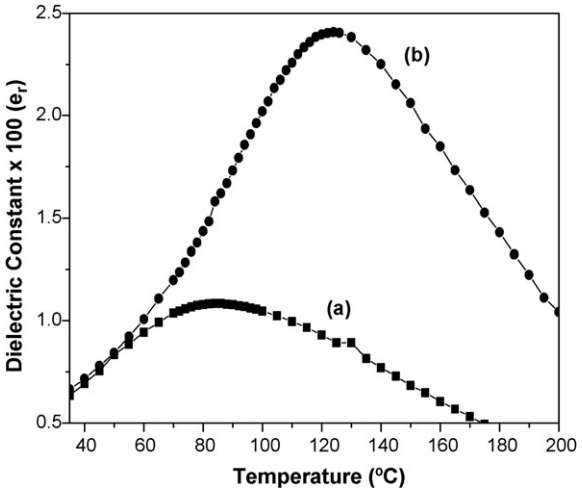

Fig. 4. Dielectric constant vs. temperature: (a) 9.5/65/35 PLZT thick film fired at 800 °C with 3 layers and (b) 9.5/65/35 PLZT hot pressed in oxygen at 1200 °C/4 h.

ders obtained by chemical synthesis method (Fig. 1). It is possible to note that the particle size does not reach 20 nm (Fig. 2).

The thick films were prepared from the mixture of functional PLZT phase, binder and low-melting crystallizable glass and after that deposited on Al_2O_3 substrates. Since the chemical stability and chemical compatibility of Al_2O_3 with the film is good, the inter-diffusion was minimized. The cross section of two-layers screen-printed PLZT films is presented in Fig. 3. The adhesion of Ag–Pd/BT electrodes was rather strong and the adhesion of the bottom and upper electrode layer overprinted were good and it could not be peeled off with scotch tape.

PLZT thick films were thermally treated at 800 °C showing rather rounded and small grains (inset in Fig. 3). The grain size of PLZT thick film is less than 1 μm, approximately 700 nm and is influenced by nanosized PLZT powders, low firing temperature and short annealing time. Low temperature melting glass frits improve PLZT rheological properties and wet the substrate. No obvious cracks are observed.

It is known that after thick film deposition, the stresses, especially tensile stresses, can produce disastrous results such as delaminating off the film from the substrate, which was not observed. The existence of small amount of porosity and traces of another phase located close to grain boundaries was probably originated from silver electrode material. On the other hand, EDX analyses of functional PLZT phase did not show the presence of liquid phase or other secondary phase more reach with Pb that is typical problem of materials based on lead.[13,14]

The dielectric constant is an intrinsic behavior of the material, meanwhile many factors during preparation of thick film could affect on the final value of dielectric properties.[15,17] The dielectric properties of PLZT thick films are presented in Fig. 4. It is indicative that the dielectric permittivity for PLZT thick films was less than for the PLZT bulk obtained by double—stage sintering in oxygen and hot pressing process that was reported in our previous published papers. The dielectric constant at room temperature (25 °C, frequency region from 1 kHz up to 100 kHz) is around 50, and no notable difference in compared to hot pressed bulk PLZT is not observed. The dielectric losses were ranging from 1.7 to 2.5×10^{-2}. However, the phase transition for thick film is not well expressed showing very broad effect caused by crystal structure of PLZT with small tetragonallity. The Curie temperature was around 85 °C in compared to well-expressed Curie temperature of hot pressed samples reaching 118 °C. Dielectric constant of PLZT thick films at the Curie temperature was ~105 comparing to 245 of 9.5/65/35 hot pressed samples. The possible reason for evident difference considering hot pressed bulk and thick film of 9.5/65/35 is most probably caused by present porosity and small grain size. So-called "grain size effects" deals with the relation of dielectric permittivity (ε) and has important influence on the properties.[8,17] It has been found that the decrease in ε is generally attributed to decrease of grain size and grain growth. On other hand, after deposition of the electrode material, based on Ag/Pd, it is assumed

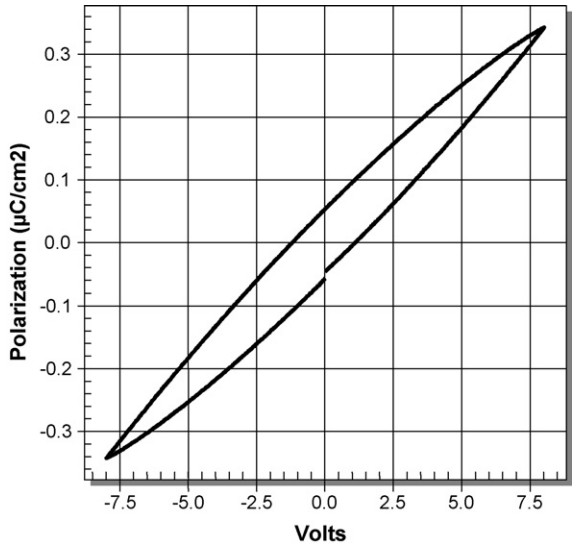

Fig. 5. Hysteresis loop for 9.5/65/35 thick films with three layers.

that part of electrode material diffuses from surface of PLZT layer into intergranular pores, forming a conductive film and changing the dielectric properties of film. The hysteresis loop of the 3 layers PLZT thick film is presented in Fig. 5. It could be noticed that the loop is well performed meanwhile it is rather narrow. The remnant polarization is 6×10^{-2} μC/cm^2 and the coercive field is 1.75 V/cm^2. The obtained results point to the small values of P_r and E_c probably caused by small grain size (grain boundary effect) and by influence of interface electrode/film.

4. Conclusion

PLZT thick films based on nanosized powders produced by soft chemistry (polymeric precursor method) were fabricated with success by screen-printing technique on Al_2O_3 substrate with PdAg/Pd as upper and bottom electrodes. The thickness is ranging from 25 to 75 μm. The adhesion electrode/support and electrode/PLZT layer was strong and no delaminating off was noticed.

The dielectric constant of 9.5/65/35 thick film is ∼105 at the Curie temperature of 85 °C. The phase transition shows a broad change that is caused by crystal structure of PLZT fired at low temperature and with small grain size. More dense films, grain growth, or other configuration of electrodes could probably diminish this fact.

The remanent polarization of 9.5/65/35 PLZT thick film was 6×10^{-2} μC/cm^2 and the coercive field was 1.75 V/cm^2. The small values of P_r and E_c are probably caused by presence of small amount of PbO beside PLZT phase, small grain size (grain boundary effect) and by the influence of interface electrode/film.

Acknowledgements

The authors gratefully acknowledge the Serbian Ministry of Science and Environmental Protection, European Scientific Foundation COST 539 and Brazilian research funding institutions FAPESP, CNPq and CAPES for the financial support during this work.

References

1. Haertling, G. H., Integrated thin films and applications. In *Ceramic Transactions*, *vol. 86*, ed. R. K. Pandley, D. E. Witter and U. Varshney, 1999, pp. 235–261.
2. Larry, J., Rosenberg, R. and Uhler, R, In: Thick Film Technology: An Introduction to the Materials, *IEEE Transactions*, 1980 [CHMT-3].
3. Brown, D. and Salt, F., Mechanism of eletrophoretic deposition. *J. Appl. Chem.*, 1963, **15**, 40–48.
4. Yamashita, K., Nagai, M. and Umegaki, T., Fabrication of green films of single and multi-component ceramic composites by eletrophoretic deposition technique. *J. Mater. Sci.*, 1997, **32**, 6661–6664.
5. Hasegawa, K., Nishimori, H., Tatsumisago, M. and Minami, T., Effect of polyacrilic acid on the preparation of thick silica films by sol–gel deposition. *J. Mater. Sci.*, 1998, **33**, 1095–1098.
6. Nicholson, P. S., Searcher, P. and Datta, S., Producing ceramic laminate composites by EDP. *Am. Ceram. Soc. Bull.*, 1996, **75**(11), 48–51.
7. Gomez-Yanez, G., Benitez, C. and Balmori-Ramirez, H., Mechanical activation of the synthesis reaction of $BaTiO_3$ from a mixture of $BaCO_3$ and TiO_2 powders. *Ceram. Int.*, 2000, **26**, 271–277.
8. Simon, L., Dren, S. L. and Gonnard, P., PZT and PT screen-printed thick films. *J. Eur. Ceram. Soc.*, 2001, **21**, 1441–1444.
9. Bouchard, R., Thick film technology: an historical perspective. In *Dielectric Ceramic Materials*, ed. K. M. Nair and A. S. Bhalla. The American Ceramic Society, Westerville, OH, USA, 1999.
10. Holc, J., Hrovat, M. and Kosec, M., Interaction between alumina and PLZT thick films. *Mater. Res. Bull.*, 1999, **34**(14/15), 2271–2278.
11. Hrovat, M., Belavic, J., Kita, J., Cilensek, J., Golonka, G. and Dziedzic, A., Thick-film temperature sensors on alumina and LTCC substrates. *J. Eur. Ceram. Soc.*, 2005, **25**, 3443–3450.
12. Laurent, M., Schreiner, U., Langjhar, P. A., Glauzunov, A. E. and Hoffman, M. J., Microstructural and electrical characterization of La-doped PZT prepared by precursor method. *J. Eur. Ceram. Soc.*, 2001, **21**, 1495–1498.
13. Stojanovic, B. D., Foschini, C. R., Zaghete, M. A., Cilense, M., Cavalheiro, A. A., Paiva-Santos, C. O. *et al.*, Microstructure of organometallic derived PLZT ceramics. *J. Eur. Ceram. Soc.*, 2001, **21**, 1491–1494.
14. Stojanovic, B. D., Zaghete, M. A., Paiva-Santos, C. O., Cilense, M., Magnani, R., Longo,. E. *et al.*, Hot-pressed 9.5/65/35 PLZT prepared by the polymeric precursors method. *Ceram. Int.*, 2000, **26**, 625–630.
15. Stojanovic, B. D., Foschini, C. R., Pavlovic, V. B., Pavlovic, V. M., Pejovic, V. and Varela, J. A., Barium titanate screen-printed thick films. *Ceram. Int.*, 2002, **28**, 293–298.
16. Stojanovic, B. D, Ristic, M. M., Pavlovic, V. B., Pavlovic, V. M., Pejovic, V., and Lekovic, M. Procedure for the preparation of dielectric pastes for thick films based on $BaTiO_3$, P-20/99, Patent YU, 12.04.2006.
17. Hrovat, M., Holc, J., Drnovsek, S., Belavic, D., Cilensek, J. and Kosec, M., PZT thick films deposited on LTCC substrate with an interposed alumina barrier layer. *J. Eur. Ceram. Soc.*, 2006, **26**, 897–900.