

Preparation and Characterization of Screen-printed Lead Zirconate Titanate Thick Films

Sung-Gap Lee^a

Department of Ceramic Engineering, Gyeongsang National University, Eng. Res. Insti., Gajwa-dong, Jinju-si, Gyeongnam 660-701, Korea

^aE-mail : lsgap@gsnu.ac.kr

(Received March 16 2006, Accepted April 5, 2006)

Ferroelectric PZT heterolayered thick films were fabricated by the alkoxide-based sol-gel method. PZT(Zr/Ti=60/40) paste was made and alternately screen-printed on the Al₂O₃ substrates. We have introduced a press-treatment to obtain a good densification of screen printed films. The porosity of the thick films was decreased with increasing the applied pressure and the thick films pressed at 0.6 ton/cm² showed the dense microstructure and thickness of about 76 μm. The relative dielectric constant increased with increasing the applied pressure. The remanent polarization and coercive field increased with increasing applied pressure and the values for the PZT thick films pressed at 0.6 ton/cm² were 16.6 μC/cm², 76.9 kV/cm, respectively.

Keywords : PZT, Ferroelectric, Thick films, Screen-printing, Structural properties

1. INTRODUCTION

Ferroelectric Pb(Zr,Ti)O₃ (PZT) material is one of the most important electronic ceramics materials for use in sensors, actuators, and filters, because of their unique properties. Interest in applying PZT films to microactuators has been increasing recently[1-3]. In most cases, films thicker than 10 μm are required to obtain a large force effectively, though the optimum thickness depends on the structure and substrate material of the actuator. Generally, PZT thick films are fabricated on substrates, such as Al₂O₃ and ZrO₂, using a screen-printing method, and sintering temperatures above 1000 °C are required to fabricate dense thick films. The screen-printing method is especially useful for a high productivity and good cost performance brings the films to the stage of commercial mass production[4,5]. It offers a batch processing opportunity and it can be used to deposit a wide range of products. Although it would be highly desirable to screen-print other components, such as capacitors, varistors, sensors, etc., currently this cannot be done while keeping the electrical properties of the corresponding ceramics. One of the main problems, inherent to this technology, is the lack of compactness of the screen printed layers[6].

In this study, PZT thick films were prepared by the screen printing techniques, in which they were screen-printed on high purity alumina substrates using PZT

(Zr/Ti=60/40) paste. We introduced a press-treatment of the green film printed on the substrates to obtain a good densification of screen printed films without inorganic binder. And the structural and dielectric properties of the thick films were investigated for fabricating various transducers and electronic devices.

2. EXPERIMENTAL

PZT(Zr/Ti=60/40) powders with excess Pb-acetate 10 mol% were prepared from Pb acetate trihydrate (Pb(CH₃CO₂)₂ · 3H₂O), Zr propoxide (Zr(OCH₂CH₂CH₃)₄) and Ti iso-propoxide (Ti[OCH(CH₃)₂]₄) as the starting materials, and 2-methoxyethanol (CH₃OCH₂CH₂OH) as the solvent using the sol-gel method[7]. Pb acetate was dissolved in 2-methoxyethanol at 90 °C, and then the solution was heated to 120 °C for the evaporation of water. After cooling to 60 °C, Zr propoxide and Ti iso-propoxide, dissolved in 2-methoxyethanol, were added to the solution. The mixed solution was refluxed and then 2-methoxyethanol and water were added to the solution for stabilization and hydrolysis, respectively. The powder precursors were dried at 100 °C for 72 h and then calcined at 850 °C for 2 h in a high purity alumina crucible. The calcined powders were ground by using planetary ball milling for 24 h.

The screen-printable pastes were prepared by kneading the ground PZT powder with 30 wt% of organic vehicle (Ferro B75001) in a non-bubbling kneader (NBK-1, Kyoto Electro.). The Pt bottom electrodes were screen-printed on the high purity alumina substrate ($15 \times 15 \times 1 \text{ mm}^3$). The PZT paste was screen-printed on the substrates and dried at $80 \text{ }^\circ\text{C}$ for 30 min. This procedure was repeated 4 times. After removal

of the solvents, the screen printed films were pressed at 0, 0.2, 0.4, 0.6 ton/cm^2 using a hydraulic press. These PZT thick films were sintered at $1050 \text{ }^\circ\text{C}$ for 2 h in PbO atmosphere. The surface and cross-sectional microstructures of films were examined using scanning electron microscopy (SEM). The upper electrodes were fabricated by screen printing the Ag paste. After poling with a field of 30 kV/cm for 30 min at $120 \text{ }^\circ\text{C}$, the dielectric properties of the specimens were measured using an LCR-meter (ANDO 4301). Ferroelectric properties were measured using a ferroelectric tester (Radiant, RT-66 A).

3. RESULTS AND DISCUSSION

Figure 1 shows the surface and cross-section SEM micro graphs of the PZT thick films printed on Pt/alumina substrate for various applied pressure. The average grain size was about $1\text{-}2 \text{ }\mu\text{m}$. The rugosity and the porosity of the thick films were decreased with increasing the applied pressure and the PZT thick films pressed at 0.6 ton/cm^2 showed the dense microstructure and thickness of about $76 \text{ }\mu\text{m}$. The apparent density of about 4.38 g/cm^3 for the unpressed PZT thick film was improved to 5.37 g/cm^3 for the thick film pressed at 0.6 ton/cm^2 .

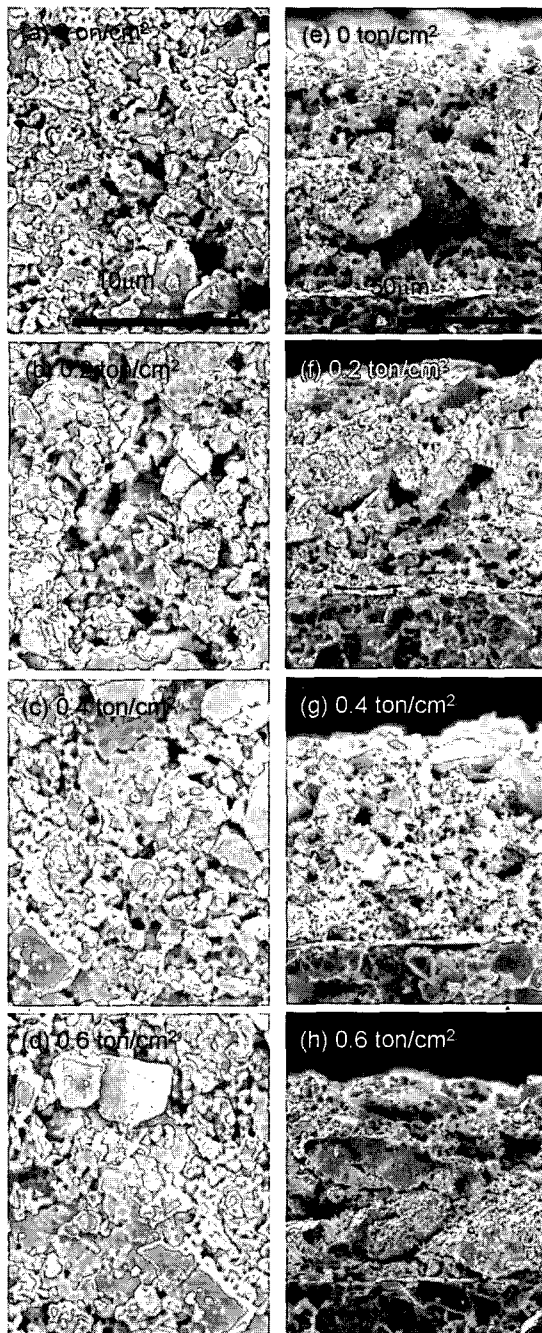


Fig. 1. Surface and cross-sectional SEM micrographs of the PZT thick films for various applied pressure.

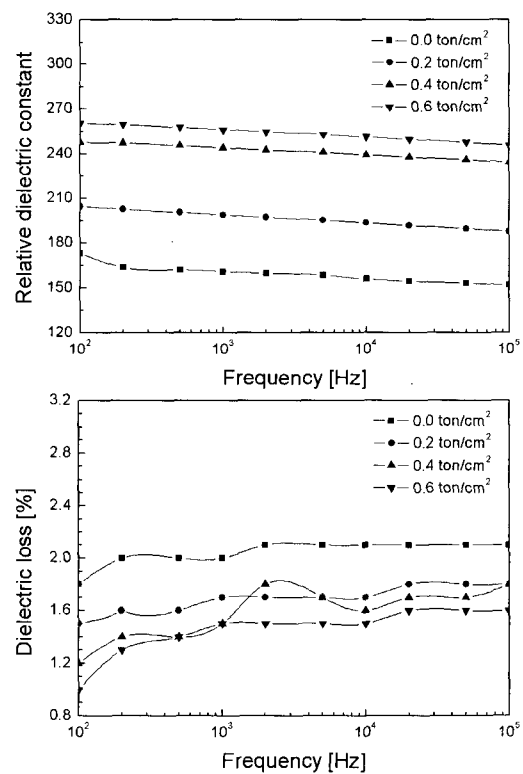


Fig. 2. Relative dielectric constant and dielectric loss of PZT thick films as a function of applied pressure and frequency.

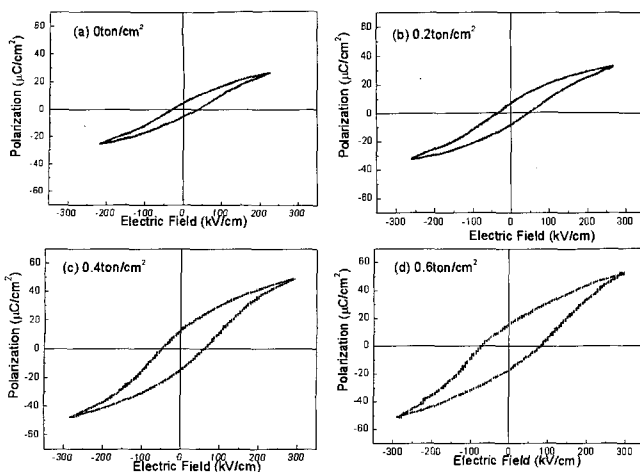


Fig. 3. P-E hysteresis loops of PZT thick films as a function of applied pressure.

Figure 2 shows the relative dielectric constant and the dielectric loss of PZT thick films with variations of applied pressure and frequency. The relative dielectric constant increased and the dielectric loss decreased with increasing applied pressure. These properties can be understood in terms of the effect of the densification and the decreasing porosity, as shown in Fig. 1. The relative dielectric constant and dielectric loss of the PZT thick films pressed at 0.6 ton/cm² were 256 and 1.50 % at 1 kHz, respectively. The dielectric constant decreased and the dielectric loss increased with an increase in the applied frequency. All specimens were showed the typical dielectric relaxation property[8].

Figure 3 and 4 show the P-E hysteresis loops and remanent polarization and coercive field of PZT thick films with variation of applied pressure, respectively. The remanent polarization and coercive field increased with an increase in an applied pressure. These properties can be understood in terms of the effect of densification and stress induced from the substrates. The porosity which created the depolarizing field decreased and the contact area of grains increased with an increase the applied pressure[9]. The remanent polarization and coercive field of the PZT thick films pressed at 0.6 ton/cm² were 16.6 μC/cm², 76.9 kV/cm, respectively. Thus, the better the densification of the films, the higher is the ferroelectric properties.

4. CONCLUSION

In this research, PZT (Zr/Ti=60/40) powders, prepared by using a sol-gel method, were mixed with an organic vehicle, and PZT thick films were fabricated by screen-printing techniques. The effect of mechanical pressure

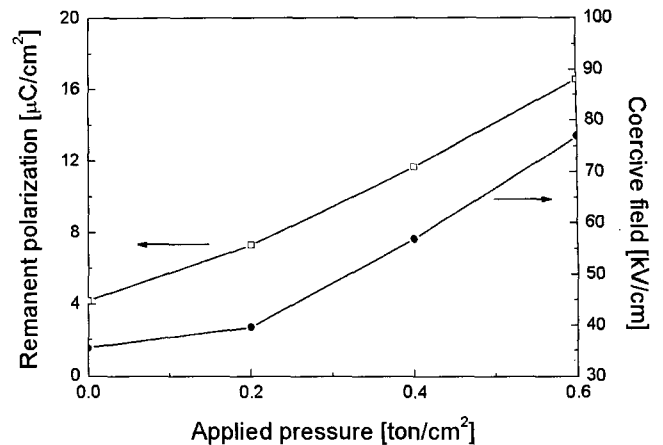


Fig. 4. Remanent polarization and coercive field of PZT thick films as a function of applied pressure.

on the electrical properties of PZT thick films has been demonstrated. The densification of the thick films was increased with increasing the applied pressure. The PZT thick films pressed at 0.6 ton/cm² showed the dense micro-structure and thickness of about 76 μm. The relative dielectric constant and dielectric loss of the PZT thick films pressed at 0.6 ton/cm² were 256 and 1.60 %, respectively. All specimens were showed the typical dielectric relaxation property. The remanent polarization and coercive field increased with an increase in an applied pressure. These properties can be understood in terms of the effect of densification and stress induced from the substrates.

ACKNOWLEDGMENTS

This work has been supported by KESRI (R-2004-B-124), which is funded by MOCIE (Ministry of commerce, industry and energy).

REFERENCES

- [1] D. Y. Jeong, S. Zhang, and H. B. Hwang, "Dependence of domain stability on the thickness of the 0.88Pb(Zn_{1/3}Nb_{2/3})O₃-0.12PbTiO₃ single crystal", J. Korean Phys. Soc., Vol. 44, No. 6, p. 1531, 2004.
- [2] K. J. Lim, J. Y. Park, J. S. Lee, S. H. Kang, and H. H. Kim, "PZT-PMN ceramics for large displacement piezoelectric devices", Trans. EEM, Vol. 5, No. 2, p. 76, 2004.
- [3] Y. J. Go, H. C. Kim, H. D. Nam, H. G. Chang, and H. Woo, "Design of the piezoelectric sounder using the PMN-PT-PZ", J. of KIEEME (in Korean), Vol. 14, No. 1, p. 12, 2001.

- [4] F. F. C. Duval, R. A. Dorey, Q. Zhang, and R. W. Whatmore, "Lead germanium oxide sinter-assisted PZT composite thick films", *J. Eur. Ceram. Soc.*, Vol. 23, p. 1935, 2003.
- [5] Y. Akiyama, K. Yamanaka, E. Fujisawa, and Y. Kowata, "Development of lead zirconate titanate family thick films on various substrates", *Jap. J. Appl. Phys.*, Vol. 38, No. 9B, p. 5524, 1999.
- [6] S. L. Dren, L. Simon, P. Gonnard, M. Troccaz, and A. Niolas, "Investigation of factors affecting the preparation of PZT thick films", *Mat. Res. Bull.*, Vol. 35, p. 2037, 2000.
- [7] S. G. Lee and Y. H. Lee, "Structural properties of PZT(80/20) thick films fabricated by screen printing method", *Trans. EEM*, Vol. 6, No. 2, p. 35, 2005.
- [8] S. G. Lee, C. I. Kim, J. P. Kim, and S. H. Lee, "Structural and dielectrical properties of barium strontium calcium titanate thick films modified with MnO₂ for phased array antennas", *Mat. Lett.*, Vol. 58, p. 110, 2003.
- [9] D. L. Corker, Q. Zhang, R. W. Whatmore, and C. Perrin, "PZT composite ferroelectric thick films", *J. Eur. Ceram. Soc.* Vol. 22, p. 383, 2002.