Structural Properties of PZT(80/20) Thick Films Fabricated by Screen Printing Method

Sung-Gap Lee[a]
Department of Ceramic Engineering, Gyeongsang National University,
Gajwa-dong, Jinju-si, Gyeongnam 660-701, Korea

Young-Hie Lee
Department of Electric and Electronic Engineering, Kwangwoon University,
447-1 Wolgye-dong, Nowon-gu, Seoul 139-701, Korea

[a]E-mail : lsgap@gsnu.ac.kr

(Received September 8 2004, Accepted March 24 2005)

$Pb(Zr_{0.8}Ti_{0.2})O_3$ powders, prepared by the sol-gel method, were mixed with an organic vehicle and the PZT thick films were fabricated by the screen-printing techniques on Pt/Al_2O_3 substrates. The structural properties were examined as a function of sintering temperature. The particle size distribution of the PZT powder derived from the sol-gel process is uniform with the mean particle size of about 2.6 m. As a result of the DTA, the formation of the polycrystalline perovskite phase was observed at around 890 °C. In the X-ray diffraction analysis, all PZT thick films showed a perovskite polycrystalline structure without a pyrochlore phase. The perovskite crystallization temperature of PZT thick films was about 890 °C. The average thickness of the PZT thick films was approximately 80-90 m.

Keywords : PZT ceramics, Thick films, Screen printing, Structural properties

1. INTRODUCTION

ABO_3 perovskite-type lead zirconate titanate ($Pb(Zr,Ti)O_3$) is one of the most important electronic ceramics materials for use in capacitors of dynamic random access memories (DRAMs), gate materials of ferroelectric RAM (FeRAM), piezoelectric transducers, pyroelectric infrared detectors and non-linear optical devices[1,2]. Among the various ferroelectrics, $Pb(Zr,Ti)O_3$ ceramics, which exhibit spontaneous polarization and a high dielectric constant, were widely investigated because of their potentials for low temperature processing and various electrical properties obtained by varying the composition ratio. Thick $Pb(Zr,Ti)O_3$ films are of major interest in the actuation of active structures in micro-electromechanical system (MEMS). Many applica-tions use their sensor or actuator capabilities in various field: medical, military, telecommunications, etc[3,4]. These applications of piezoelectric/electrostrictive materials often require dense and thick micropatterned films with a thickness of more than 10 m and low process temperature.

On one hand, the thickness of the films resulting from the usual technologies of their films deposition does not exceed a few microns and on the other hand bulk materials are hard to be manufactured with a thickness less than 100 m. The various film preparation methods for $Pb(Zr,Ti)O_3$ family were improved during the development of ferroelectric memory devices, and the resultant films were usually less than 1 m-thick. There are some reports on fabrication of $Pb(Zr,Ti)O_3$ thick films by sol-gel method[5], screen printing method[6], sputtering method[7] and hydrothermal synthesis method [8]. The screen printing technology appears like a competitive and flexible way to reach that range of thickness at a low cost. It offers a batch processing opportunity and it can be used to deposit a wide range of products.

In this study, $Pb(Zr,Ti)O_3$ thick films were prepared by the screen printing techniques on common alumina substrates, and the structural properties of the thick films were measured with variation of sintering temperature for fabricating various transducers and electronic devices

2. EXPERIMENTAL PROCEDURE

The chemical composition of the sample is given by the formula $Pb(Zr_{0.8}Ti_{0.2})O_3$(PZT). PZT powders were prepared from Pb acetate trihydrate($Pb(CH_3CO_2)_2\ 3H_2O$)

Zr propoxide($Zr(OCH_2CH_2CH_3)_4$) and Ti iso-propoxide ($Ti[OCH(CH_3)_2]_4$) as the starting materials, and 2-methoxyethanol($CH_3OCH_2CH_2OH$) as the solvent using the sol-gel method. 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.). High purity alumina was used as a substrate. The bottom electrodes were prepared by screen printing Pt paste and firing at 1450 °C for 20 min. After screen printing the PZT paste using a 200 mesh screen mask, printed films were allowed to level for 10 min and then dried at 80 °C for 30 min. These processes from printing to drying were repeated several times. The thick films were sintered at 950-1100 °C for 2 h in PbO atmosphere. The upper electrodes were fabricated by screen printing the Ag paste and then firing at 850 °C for 30 min. A powder of the dried gel was used for DTA under flowing dry air on a Shimadzu DT-40H at a constant heating rate of 10 °C/min. X-ray diffraction (XRD) and scanning electron microscopy (SEM) were introduced in order to analyze the crystallinity and the microstructure of PZT thick films, respectively.

3. RESULTS AND DISCUSSION

The particle size distribution was measured by particle size analyzer (UPA-150, USA). The particle size distribution and morphology of a PZT powder are shown in Fig. 1 and 2, respectively. It can be seen that the particle size distribution of the PZT powder derived from the sol-gel process is uniform with the mean particle size of about 2.6 m. This was confirmed by SEM examination, Fig. 2.

Figure 3 shows the differential thermal analysis (DTA) curves of the calcined PZT(80/20) powders. An endothermic peak due to the evaporation of absorbed water and solvent was observed at around 250 °C. Due to the combustion of light organic residues and acetates were observed in the temperature range of 270 to 350 °C. The endothermic peak due to the decomposition of intermediate phase formed at calcining process was observed at around 500 °C. Due to the formation of the polycrystalline perovskite phase, exothermic peak was observed at around 890 °C.

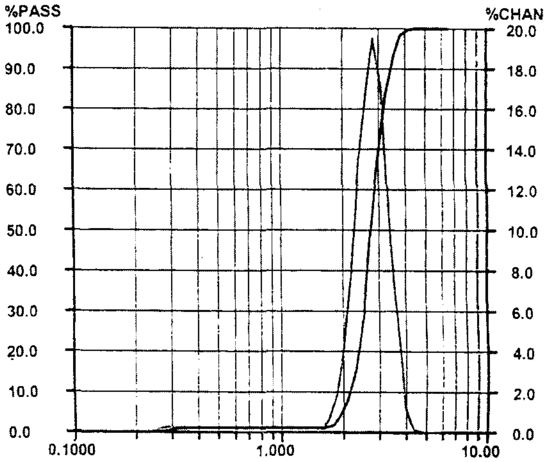

Fig. 1. Particle size distribution of the PZT(80/20) powder derived from the sol-gel process.

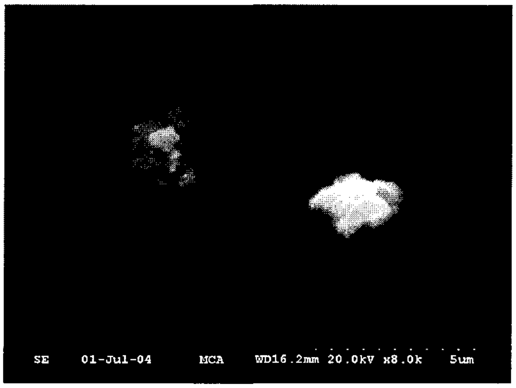

Fig. 2. SEM micrograph of the PZT(80/20) powder.

Figure 4 shows the X-ray diffraction patterns of the PZT(80/20) thick films printed on Pt/alumina substrate with variation of sintering temperature. All PZT thick films showed the typical XRD patterns of a perovskite polycrystalline structure without preferred orientation and no pyrochlore phase is observed.

Figure 5 shows the surface and cross-sectional SEM micrographs of the PZT(80/20) thick films printed on Pt/alumina substrate for various sintering temperature. The PZT thick films sintered at 950 °C exhibited an agglomerated microstructure composed of fine grains with large voids. The grain growth with non-uniform grain structure was observed above 1000 °C. Uniform grain structure and the decrease in porosity were observed with the increase in sintering temperature. But, the PZT(80/20) thick film sintered at 1100 °C showed a large size pores due to the evaporation of PbO. The adhesion between Pt and PZT is good. The average thickness of the PZT(80/20) thick films sintered at above 1000 °C was approximately 80-90 μm.

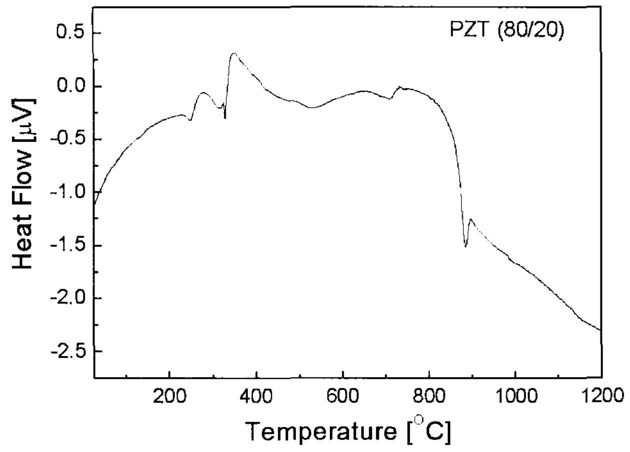

Fig. 3. DTA curve of the calcined $Pb(Zr_{0.8}Ti_{0.2})O_3$ powder.

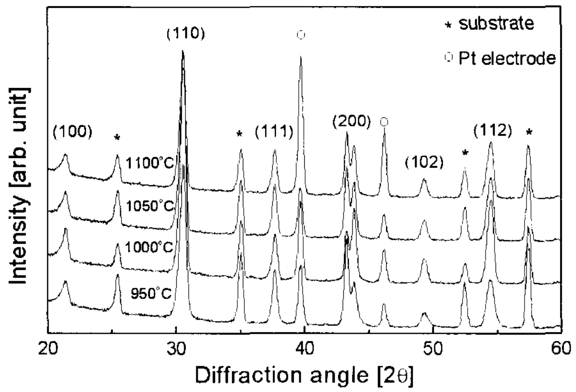

Fig. 4. X-ray diffraction patterns of the PZT(80/20) thick films printed on Pt/alumina substrate with variation of sintering temperature.

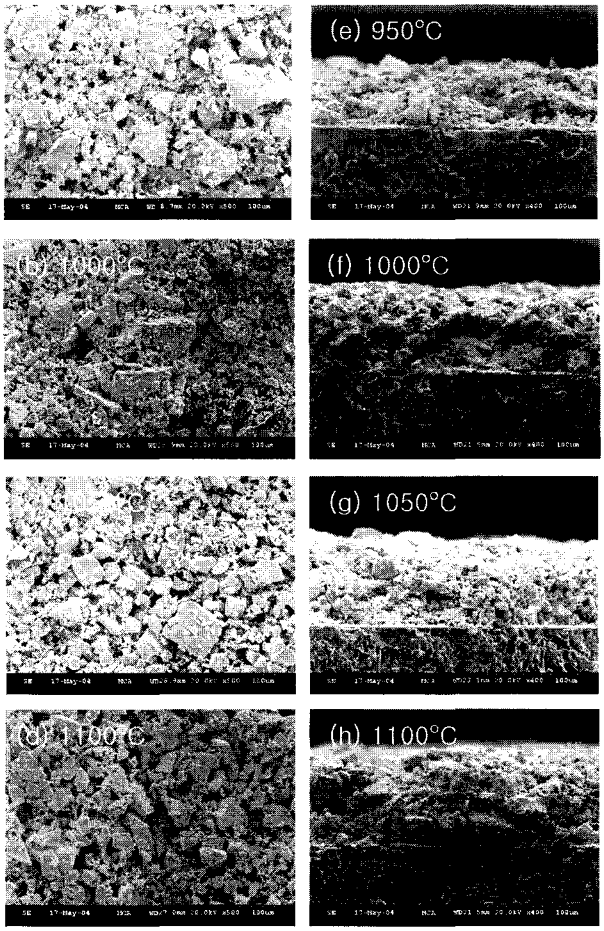

Fig. 5. SEM micrographs of surface morphologies [(a)~(d)] and cross-sections [(e)~(h)] in PZT(80/20) thick films with variation of sintering temperature.

4. CONCLUSION

In this research, $Pb(Zr_{0.8}Ti_{0.2})O_3$ powders, prepared by using a sol-gel method, were mixed with an organic vehicle, and PZT thick films were fabricated on alumina substrates by using a screen printing techniques. The structural properties were investigated for various sintering temperature. The particle size distribution of the PZT powder derived from the sol-gel process is uniform with the mean particle size of about 2.6 μm. As a result of the DTA, the formation of the polycrystalline erovskite phase was observed at around 890 °C. In the X-ray diffraction analysis, all PZT thick films showed a perovskite polycrystalline structure without a pyrochlore phase. The perovskite crystallization temperature of PZT thick films was about 890 °C. The PZT thick films sintered at 950 °C exhibited an agglomerated microstucture composed of fine grains with large voids. And the grain growth with non-uniform grain structure was observed above 1000 °C.

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 $0.88Pb(Zn_{1/3}Nb_{2/3})O_3$-$0.12PbTiO_3$ single crystal", J. Korean Phys. Soc., Vol. 44, No. 6, p. 1531, 2004.
[2] J. W. Hyun, "Electrical properties of lead magnesium tantalate-lead zirconate perovskite ferroelectrics", J.

Korean Phys. Soc., Vol. 44, No. 2, p. 381, 2004.

[3] Y. J. Go, H. C. Kim, H. D. Nam, H. G. Chang, and H. Woo, "Design of the piezoelectric sounder using the PMM-PT-PZ", J. of KIEEME(in Korean), Vol. 14, No. 1, p. 12, 2001.

[4] 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.

[5] B. H. Kim, J. H. An, K. S. Hwang, B. A. Kang, K. Nishio, and T. Tsuchiya, "AFM analysis of chemical-solution-derived epitaxial PZT films prepared by using oxidizing or non-oxidizing yrolysis", J. Korean Phys. Soc., Vol. 44, No. 2, p. 346, 2004.

[6] V. Walter, P. Delobelle, P. L. Moal, E. Joseph, and M. Collet, "A piezo-mechanical characterization of PZT thick films screen-printed on alumina substrate" Sensors and Actuators A, Vol. 96, p. 157, 2002.

[7] R. Thomas, S. Mochizuki, T. Mihara, and T. Ishida, "Influence of sputtering and annealing conditions on the structure and ferroelectric properties of Pb $(Zr,Ti)O_3$ thin films prepared by RF magnetron sputtering", Jpn. J. Appl. Phys., Vol. 40, No. 9B, p. 5511, 2001.

[8] T. K. Mandal and S. Ram, "Synthesis of $PbZr_{0.7}Ti_{0.3}O_3$ nanoparticles in a new tetragonal crystal structure with a polymer precusor", Materials Letters Vol. 57, p. 2432, 2003.