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Structural and Dielectric Properties of $Pb(Zr_{0.2}Ti_{0.8})O_3$ Thick Films Fabricated using a Screen Printing Technologies

Sung-Gap Lee[1,a] and Young-Jae Shim[1]

Abstract

$Pb(Zr_{0.2}Ti_{0.8})O_3$ 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/alumina substrates. The structural and dielectric properties were examined as a function of sintering temperature. The particle size distribution of the powder is bimodal with the mean particle size of about 1.2 μm. The average grain size of the PZT thick films sintered above 1000 ℃ was about 3.1 μm and the thickness of the specimens was approximately 41 μm. The relative dielectric constant and dielectric loss of the thick films sintered at 1050 ℃ were 337 and 1.24 %, respectively.

Key Words : PZT ceramics, Thick films, Screen printing, Structural properties, Dielectric properties

1. INTRODUCTION

ABO_3 perovskite-type lead zirconate titanate ($Pb(Zr,Ti)O_3$) is one of the most important electric 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]. $Pb(Zr,Ti)O_3$ 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. Recently, an effective and reliable technology for fabrication of actuators made of piezoelectric thick films is required as a part of the manufacture of micropumps, ultrasonic mixers in micro electromechanical systems (MEMS) and micrototal analysis system (μ-TAS), micromanipulators for medical applications, ink-jet printer heads, flapper actuators for high-density hard-disk drive, and others, which need large strain and high-speed response[3]. These applications of piezoelectric/electrostrictive materials often require dense and thick micropatterned films with a thickness of more than 10mm and low process temperature.

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 1mm-thick. There are some reports on fabrication of $Pb(Zr,Ti)O_3$ thick films by sol-gel method, screen printing method, sputtering method and hydrothermal synthesis method[4]. 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. 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.

1. Dept. of Ceramic Engineering, Gyeongsang National University
(Gazwa-dong 900, Jinju-si, Gyeongnam, Korea)
a. Corresponding Author : lsgap@gsnu.ac.kr
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2. EXPERIMENTAL PROCEDURES

$Pb(Zr_{0.2}Ti_{0.8})O_3$ powders were prepared from Pb acetate trihydrate ($Pb(CH_3CO_2)_2 \cdot 3H_2O$), Zr propoxide ($Zr(OCH_2CH_2CH_3)_4$) and Ti iso-propo -xide ($Ti[OCH(CH_3)_2]_4$) as the starting materials, and 2-methoxyethanol ($CH_3OCH_2CH_2$ OH) as the solvent using the sol-gel method. Pb acetate was dissolved in 2-methoxyethanol, and then the solution was heated for the evaporation of water. After cooling, 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 and then calcined at 850 ℃ for 2 h in a alumina crucible.

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 ℃ for 20 min. After screen printing the PZT paste using a 200 mesh screen mask, printed films were allowed to level for 10min and then dried at 80 ℃ for 30 min. These processes from printing to drying were repeated four times. The thick films were sintered at 950-1100 ℃ for 2 h in PbO atmosphere. The upper electrodes were fabri-cated by screen printing the Ag paste and then firing at 850 ℃ for 30 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. The dielectric constant and dielectric loss of the specimens were measured using a LCR- meter (ANDO 4301) at 1 KHz.

3. RESULTS AND DISCUSSION

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 bimodal with the mean particle size of about 1.2 μm. The nature of the size distribution implied an agglomerated powder. This was confirmed by SEM examination, which revealed agglomerates several microns in size, composed of micron and sub-micron sized primary particles, Fig. 2.

Figure 3 shows the differential thermal analysis(DTA) curves of the calcined PZT powders. An exothermic peak due to the decomposition of light organic and acetates was

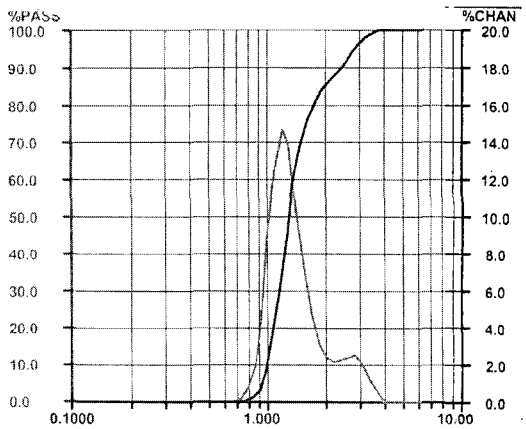

Fig. 1. Particle size distribution of the PZT powder derived from the sol-gel process.

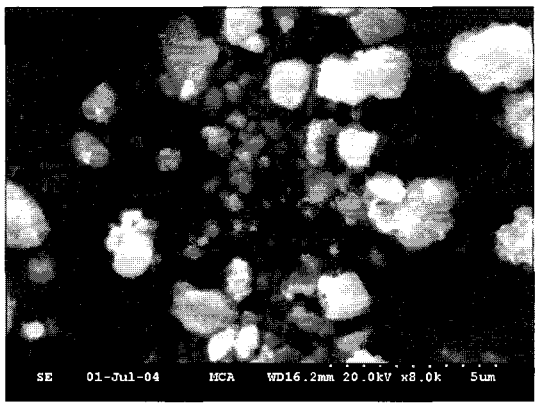

Fig. 2. SEM micrograph of the PZT powder.

observed at around 280 ℃. The endothermic peaks due to the evaporation of solvent and the decomposition of intermediate phase formed at calcining process were observed at around 320 ℃ and 475 ℃, respectively. Due to the formation of the polycrystalline perovskite phase, exothermic peak was observed at around 890 ℃.

Figure 4 shows the X-ray diffraction patterns of the PZT 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 a pyrochlore phase.

Figure 5 shows the surface and cross-sectional SEM micrographs of the PZT thick films printed on Pt/alumina substrate for various sintering temperature. The PZT thick films sintered at 950 ℃ exhibited an agglomerated micro-structure composed of fine grains with large voids. The average grain size sintered at above 1000 ℃ was about 3.1 μm. The decrease in porosity was observed with the increase in sintering

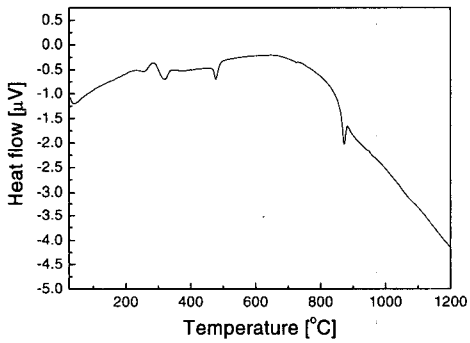

Fig. 3. DTA curve of the calcined PZT powder.

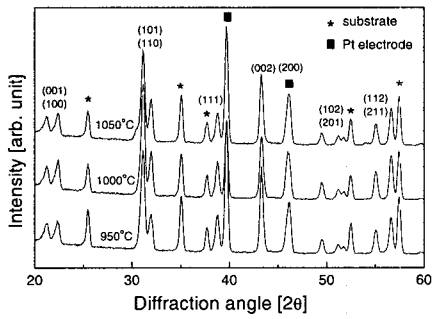

Fig. 4. X-ray diffraction patterns of the PZT thick films printed on Pt/alumina substrate with variation of sintering temperature.

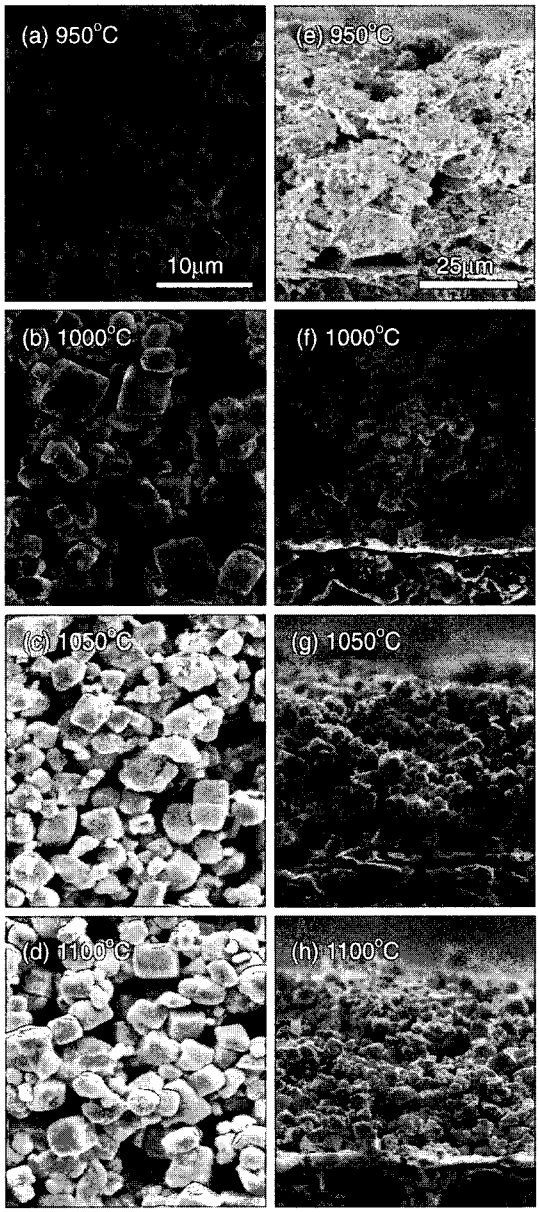

Fig. 5. SEM micrographs of surface morphologies [(a)~(d)] and cross-sections [(e)~(h)] in PZT thick films with variation of sintering temperature.

temperature. The adhesion between Pt and PZT is good. The thickness of the PZT thick films was approximately 41 μm.

After poling with a field of 20 kV/cm for 20 min at 120 ℃, the dielectric properties were measured using a LCR-meter at 1 kHz. Figure 6 shows the relative dielectric constant and the dielectric loss of PZT thick films with variation of sintering temperature. The relative dielectric constant increased and the dielectric loss decreased with increasing sintering temperature until 1050 ℃. These properties can be understood in terms of the effect of the grain growth and the decreasing porosity, as shown in Fig. 5. The relative dielectric constant and dielectric loss of the PZT thick films sintered at 1050 ℃ were 337 and 1.24 %, respectively. But, in the PZT thick films sintered at 1100 ℃, the relative dielectric constant decreased and the dielectric loss increased due to PbO evaporation at high sintering temperature.

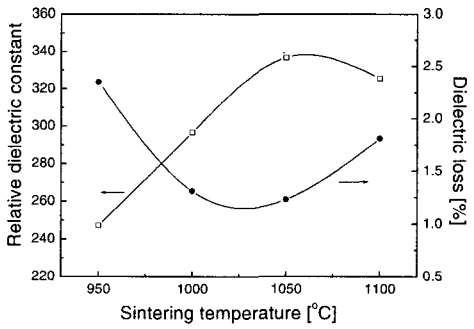

Fig. 6. Relative dielectric constant and dielectric loss of PZT thick films at 1 KHz as a function of sintering temperature.

4. CONCLUSIONS

In this research, $Pb(Zr_{0.2}Ti_{0.8})O_3$ powders, prepared by using the sol-gel method, were mixed with an organic vehicle, and PZT thick films were fabricated on alumina substrates by using screen printing techniques. The structural and the dielectric properties were investigated for various sintering temperature. 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 ℃. The PZT thick films sintered at 950 ℃ exhibited an agglomerated microstructure composed of fine grains with large voids. The relative dielectric constant increased and dielectric loss decreased with sintering temperature until 1050 ℃. These properties can be understood in terms of the effect of grain growth and the decreasing porosity.

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REFERENCES

[1] Y. H. Son, K. T. Kim, and C. I. Kim, "Ferroelectric properties of Tb-doped PZT thin films prepared by sol-gel process", J. of KIEEME(in Korean), Vol. 17, No. 9, p. 947, 2004.

[2] J. H. Park, "Characterization of ferroelectric thin films in microwave region", J. of KIEEME(in Korean), Vol. 17, No. 9, p. 947, 2004.

[3] 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 pyrolysis", J. Korean Phys. Soc., Vol. 44, No. 2, p. 346, 2004.

[4] Y. Ohba, M. Miyauchi, T. Tsurumi, and M. Daimon, "Analysis of bending displacement of lead zirconate titanate thin film synthesized by hydrothermal method", Jpn. J. Appl. Phys., Vol. 32, No. 9B, p. 4095, 1993.