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Characterization of Thick Film Piezoelectric Lead Zirconate Titanate (PZT) Ceramics Fabricated By Tape Casting Processing

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Abstract—**Microstructures and electrical properties of PZT thick films fabricated by using a tape casting processing have been studied. The PZT thick film elements sintered at 1250-1300 °C. The PZT thick film obtained shows a uniform grain size and very dense microstructure with minimal pores and better than most of the screen-printed film reported before. A piezoelectric constant d_{31} of about -181pm/V was derived from the measurement of a unimorph actuator (23µm PZT/110µm stainless steel foil), which was very close the measurement results of thicker films. This proves that PZT films can be fabricated down to tens of micrometer with similar piezoelectric coefficients to bulk ceramics. The characterization results show tape-casting processing can be used to fabricate high quality PZT thick film resonators, and the extracted material constants can be used for sensor, actuator and transducer design.**

Keywords-PZT thick films; tape casting

I. INTRODUCTION

Based on the outstanding dielectric, piezoelectric and ferroelectric properties, lead zirconate titanate (PZT) thick films and ceramics have been widely used in microelectromechanical applications such as nonvolatile memories, microsensors and microactuators, and ultrasonic transducers [1-5]. In many transducer applications, particularly for high frequency ultrasonic transducers, PZT thick films are necessary with thickness from 10µm to 100µm because they can provide larger force, higher sensitivity, and broader working frequency range compared to thin films [4, 5]. However, fabrication of high quality PZT thick film has been a challenge by traditional ceramic processing, sol-gel spin-on coating, and ceramic slurry screen printing approach. PZT thin sheet with thickness down to 100µm can be fabricated by mechanical dicing method using bulk ceramic PZTs, but with some degree of surface damage during cutting process. Sol-gel spin-on coating is a slow processing, with multiple coating and annealing steps, PZT thick films up to 10 µm have been fabricated [6-8]. But it is hard to maintain the processing consistency and compositional stoichiometry; and the property variation happens for each batch. Screen printing of thick film PZTs with thickness from 10µm to 100µm usually lead to a low electromechanical property owing to the low sintering temperature and the use of sintering aids [6]. Therefore, we adopted tape-casting processing to fabricate PZT thick film. Tape-casting processing has been used for multilayer capacitor fabrication for a few decades [3].

Tape casting is an important ceramic forming technique widely used in the production of thin sheets of flexible tape. When initially developed more than 50 years ago, the tape casting process enabled production of ceramic capacitors with the improved dielectric properties and smaller footprints required by the emerging microelectronics industry. Tape casting is a straightforward method of forming uniformly thin sheets of film that is inexpensive, scalable, and may be used with any ceramics, metals, or polymers that are readily mixed in a liquid suspension or slip.[6,7] Tape-casting processing has been proved to be a standard processing technique for thick film ceramic. In this study, we have successfully fabricated PZT thick films with different compositions by using tape-casting processing to form sheet PZT green layers, followed by sintering at appropriate temperatures to obtain high density and flexible PZT ceramics with thickness from 10µm to several hundred µm. The material properties of thick PZT films were adjusted by compositions and by controlling tape-casting process parameters.

II. EXPERIMENTAL

The tape casting PZT thick-film ceramics are fabricated with compositions near morphotropic phase boundary (MPB). The large number of polarization directions enables optimized crystallographic orientations to be established from grain to grain in the poling process and, in turn, results in anomalously high piezoelectric properties. Further improvements are made to the electromechanical properties through compositional modifications. The grain size effect also plays an important role on the piezoelectric and dielectric properties [7]. The processing started with the preparation of PZT ceramics with Zr/Ti ratio of 52/48, with additives such as Lanthanum oxide and Niobium oxide. The raw materials PbO, ZrO2, and TiO2 and additives were mixed with appropriate compositions by ball billing, followed by drying, calcinations and fine vibratory

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milling to form PZT powders with average particle size at submicrons. For tape casting, the slip contains the ceramic powder, an organic binder, and other organic additives such as plasticizers, dispersants, and deforming agents. In the case of using aqueous binders, slurry is prepared by adding PZT powder (75-78wt.%) with deionized water (21-24wt.%) and dispersant (0.8-1wt.%) and followed by milling. The milled slurry was then added with dispersant (33% TRITON-100 solution in de-ionized water) and wet agent (33% TRITON CF-10) supplied by Sigma Chemical, and the Dow Chemical Company. Then the milled slurry solution (85wt.%) was added with ammoniated 5310 and 5320 acrylic resins (7.5wt.% each) to form the slip for tape casting. In the case of using non-aqueous binder system, the binder mix formulation consists of 43wt.% binder polymer solution (acrylic resin), 3wt.% plasticizer (Santicizer 160, butyl benzyl phthalate), and 54wt.% solvent (1.1.-trichlorethane). The slip was prepared by adding PZT powders with binder mix. After slip preparation and de-air steps, the PZT green tape sheet with appropriate thickness is casted by a customized belt-casting system using stainless steel belt. PZT sheets with thickness from 0.4 to 4 mils (10 to 100 mm) have been prepared. Medium to high green strength has been obtained by carefully control the processing conditions. After the PZT green tape is fabricated, rectangular and circular shaped PZT green sheet were cut or punched to desirable dimensions or diameters, followed by high temperature binder burnout at about 500^{o}C and sintering at higher temperature to form PZT thick film ceramics [8].

Figure 1 shows the SEM microstructure of a PZT thick film with about 20µm thickness with the sintering condition of 1250-1300 oC. Clearly, the PZT thick film obtained shows a uniform grain size and very dense microstructure with minimal pores and better than most of the screen-printed film reported before. Thin silver electrodes were coated by screen printing and cured at 650°C. The electroded PZT ceramics were then subjected to poling at 3kV-5kV/mm electrical strength to induce the piezoelectric activity. Figure 2 shows the photos of PZT thick film used for property characterization in this work.

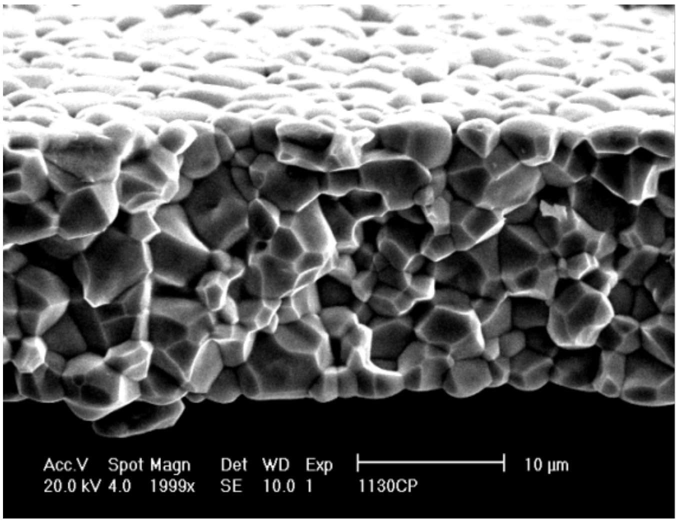

Figure 1. SEM microstructure of dense PZT thick film fabricated by tape-casting processing.

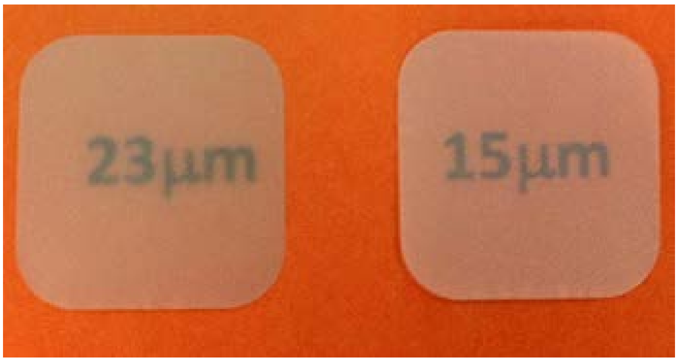

Figure 2. The fabricated PZT thick film

III. MESUREMENT OF PZT THICK FILM AND RESULTS

The frequency spectrum of PZT thick film was first characterized using an Agilent 4294A precision impedance analyzer (Agilent Technologies, Santa Clara, CA). Figure 3 shows the measured impedance spectrum of PZT thick film within a frequency range from 200Hz to 600Hz, and a resonance frequency point f_0= 406Hz was found, which corresponds to the first order longitudinal resonance frequency of the piezoelectric thick film.

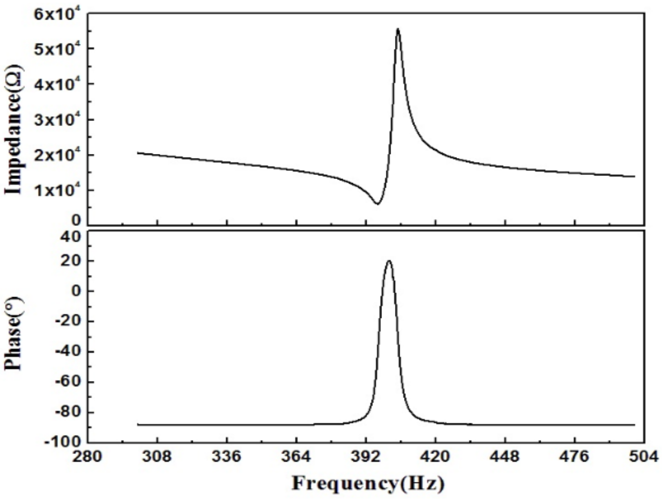

Figure 3. Impedance spectrum of the piezoelectric thick film

In order to measure the piezoelectric properties, very thin gold electrodes (80-120 nm) were coated by DC sputtering using a sputter coater to reduce the electrode effect of the PZT resonators for the electroemechanical materials property characterization. Long strip shaped PZT thick-film elements were also prepared using the tape casting method, with thickness of 23µm, a width of about 2mm, and length of

15.85mm. The electroded PZT ceramics were then subjected to poling at 60V for 1min electrical strength to induce the piezoelectric activity. The PZT thick-film cantilever beam was prepared by bonding the PZT thick-film element to a stainless steel foil with similar lateral dimension, but with a thickness of about 115µm, using a very thin epoxy bonding. Shown in Figure 4 is a set- up photo taken during experimental processing to measure the tip displacement. One end of the PZT thick-film cantilever was mechanically clamped using a special fixture. [9]

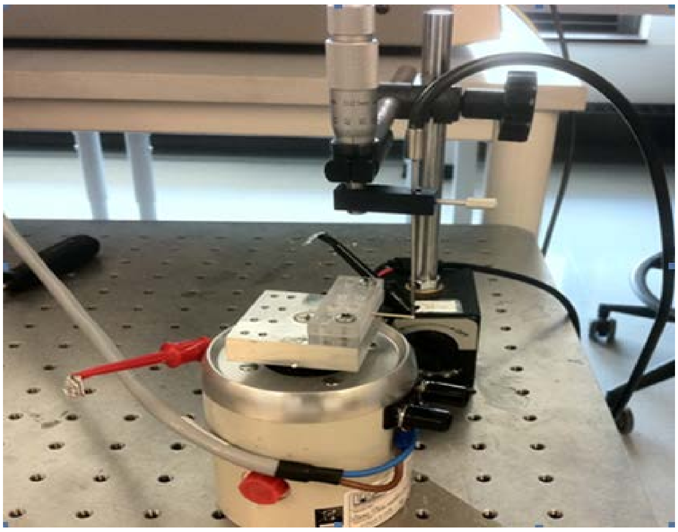

Figure 4. set- up photo taken during experimental processing to measure the tip displacement

Figure 5 is the tip displacement of a PZT thick-film stainless steel unimorph actuator with length of 15.85mm and PZT thickness of 23µm, measured by using microdisplacement measurement system (MTI 2000 Fotonic Sensor). It shows a strict linear relationship between the driving voltage and the tip displacement.

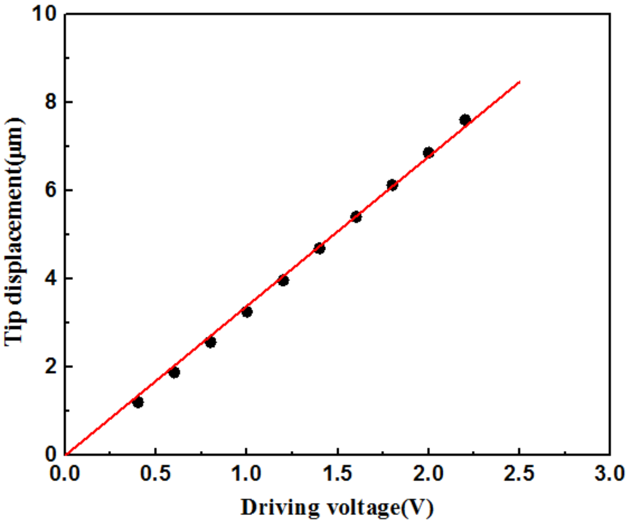

Figure 5. Applied voltages and tip displacement relationship for a PZT thick film/stainless steel unimorph actuator.

The piezoelectric constant was extracted by the measurement of tip displacement of actuators and following the equation [10]:

$$\delta = \frac{3L^2}{2t_p}\frac{2AB(1+B)}{A^2B^4+2A(2B+3B^2+2B^3)+1}d_{31}E_3 \qquad (1)$$

where L is the effective length of the unimorph actuator, t_p is the PZT thickness, $E_3=V/t_p$ is the applied field and V is the applied voltage, $A=Y_m/Y_p$ is the Young's modulus ratio of stainless steel to PZT($Y_p=1/S_{11}^E$ and S_{11}^E is assumed with same value with thick film), and $B=t_m/t_p$ is the thickness ratio of stainless steel to PZT. Using this relationship and the data given in Figure 5, the piezoelectric constant d_{31} of the laser transferred PZT thick film was derived, which is −181 pm/V. This demonstrated the piezoelectric properties of the PZT thick films obtained here are higher than the screen-printing PZT thick films reported in the literature, where the piezoelectric constant d_{31} in PZT ceramics is -124pm/V.

IV. CONCLUSIONS

In summary, PZT thick films have been successfully fabricated using tape-casting processing. Their microstructures and properties were studied. The PZT thick film elements sintered at 1250-1300 °C. The PZT thick film obtained show a uniform grain size and very dense microstructure with minimal pores and better than most of the screen-printed film reported before. A piezoelectric constant d_{31} of about -181pm/V was derived from the measurement of a unimorph actuator (23µm PZT/110µm stainless steel foil), which was very close the measurement results of thicker films. This proves tape-casting method can be used to fabricate PZT films down to several tens of micrometer with high quality piezoelectric properties. Tape-casting method has been shown as a useful way to fabricate high quality lead zirconate titanate (PZT) thick films with controllable material properties, and can be used for sensor, actuator and transducer design and applications.

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