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# High performance screen printed $Pb(Zr_{0.46}Ti_{0.54})O_3-Pb(Zn_{1/3}Nb_{2/3})O_3-Pb(Ni_{1/3}Nb_{2/3})O_3$ thick films by one-step co-firing method

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ABSTRACT

High performance screen-printed PNN – PZN – PZT thick films have been successfully prepared using a new one-step co-firing method at relatively low sintering temperature, leaving out preceding binder removal and subsequent electrode-made processes. And the dependence of microstructure, densification and electrical properties on the content of sintering aids has been investigated. The specimens with 1 wt % sintering aids sintered at 850 °C exhibits markedly enhanced piezoelectric and dielectric properties: $d_{33}=202$ pC/N, $\varepsilon_{33}^T/\varepsilon_0=987$, $\tan\delta=1.8\%$, $Tc=295$ °C, and $Pr=14.02$ μC/cm$^2$. Furthermore, there is no obvious Ag diffusion into PZT thick films, indicating the favorable coherence. Such prominent properties of PZN – PNN – PZT thick films using one-step co-firing method can be applied to multilayer thick films and further MEMS device applications.



## 1. Introduction

With the advent of the MEMS (micro-electromechanical system), there are conflicting desires for miniaturization and integration of electronic devices [1,2]. Piezoelectric thick films with the thickness of 10–100 μm fill the gap between processing capabilities of thin films and bulk ceramics and combine their advantages of larger actuating force and displacement, lower working voltage, wider working frequency and compatibility with semiconducting integrated circuit [3–5]. Consequently, PZT thick films have been promisingly applied to micromotors, ultrasonic transducers and energy harvesters.

Screen-printing processes offer many advantages in precise control of thickness and chemical composition of films, totally compatibility with MEMS technology, and low-cost for large-scale production, when compared with other processes such as electrophoretic deposition, aerosol deposition and sol-gel [4,6,7]. However, most of previous reports on screen-printed thick films did not pay much attention to co-firing method and separately finished organic binder removal, PZT sintering and electrode-made processes. Besides, they mostly used expensive metals like Au, Pt or Ag – Pd as electrodes, and some even adopted electrode sputtering method. Tedious steps of sintering process would lead to diffusion and reaction between electrode and thick films especially when screen-printing method is adopted. All these would cause high energy consumption and manufacturing cost [8,9]. Moreover, most of high-performance specimens were sintered at relatively high temperature, which was unacceptable for Ag electrode. Sintering temperature above 850 °C would result in Ag diffusion into thick films and deteriorated properties [10].

To solve these drawbacks, we use Ag as electrode and introduce a simple one-step co-firing method which means finishing the binder removal, PZT sintering and electrode sintering processes at the same annealing process. With this technique, optimal $d_{33}$ of PNN – PZN – PZT thick films is 202 pC/N, which is much higher than screen-printed thick film specimens sintered at similar sintering temperature. Furthermore, the ultimate goal of one-step co-firing thick films is to lay a foundation for the processing of multilayer PZT ceramics and further MEMS device applications.

## 2. Experiment

The screen printed PZT thick film specimens on aluminum substrate were fabricated by one-step co-firing method. The $0.7Pb(Zr_{0.46}Ti_{0.54})O_3-0.1Pb(Zn_{1/3}Nb_{2/3})O_3-0.2Pb(Ni_{1/3}Nb_{2/3})O_3$ raw powders were calcined at 850 °C by conventional solid-state reaction method. Sintering aids consisting of $Pb_3O_4$, $H_3BO_3$, $SiO_2$ and $Al_2O_3$ (15:2:7:1) were mixed with PZT powders to reduce the sintering temperature. The processed powders were ball-milled for 10 h to obtain submicron particle size. Screen printing paste prepared by mixing the powders and organic vehicle consisting of triethanolamine, ethyl-cellulose and terpinol. PZT paste was printed on alumina substrate with screen-printed Ag bottom electrode, and dried at

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120 °C for 10 min. This process was repeated for 8 times. Top Ag electrode was printed on dried thick film. Printed specimens were sintered at 800–900 °C for 90 min with intermediate 400 °C holding for 1 h to remove organic binders. The specimens were poled in silicone oil at 120 °C with a DC field of 6.0 kV/mm for 10 min. The properties were measured after aging for 24 h.

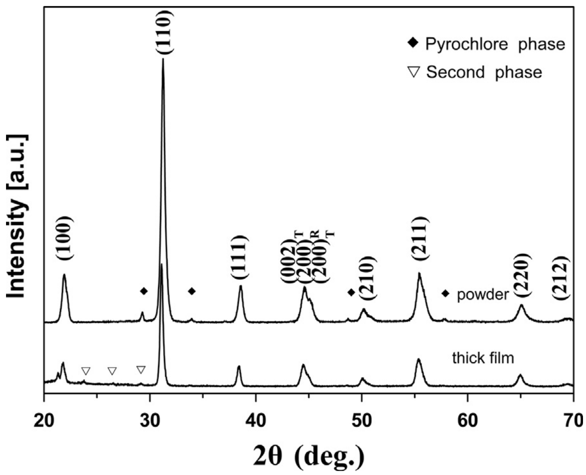


**Fig. 1.** X-ray diffraction pattern of PZN–PNN–PZT powders and thick films synthesized and sintered at 850 °C.

The crystalline phase and micro-structural information was investigated by X-ray diffraction (XRD) with Cu Kα radiation (D/MAX-2500, Rigaku, Tokyo, Japan) and scanning electron microscopy (SEM: Hitachi S-4800, Osaka, Japan), respectively. The dielectric properties were measured with an LCR automatic meter (XC2810A, Tianjin XinCe Electronics Appartaus Technology Co., Ltd., Tianjin, China). The piezoelectric coefficients were measured by a quasistatic piezoelectric $d_{33}$ meter (ZJ-2, Institute of Acoustics Academic Sinica, Beijing, China). P–E hysteresis loops were determined by a standard ferroelectric tester (WS-2000, Tsinghua University, Beijing, China) at a frequency of 1 kHz.

## 3. Results and discussions

Synthesis of powders preliminarily forms perovskite structure and improves reactivity and uniform dispersion of ions, which are important for crystallization and densification of thick films in sintering process. Fig. 1 shows X-ray diffraction pattern of PZN–PNN–PZT powders without sintering aids and thick films in which sintering aids were added respectively synthesized and sintered at 850 °C. The splitting of $(002)^T$, $(200)^R$ and $(200)^T$ peaks near 44° indicates the existence of the MPB between rhombohedral and tetragonal phase at room temperature, which is favorable for obtaining high-performance thick films. Furthermore, pyrochlore phase in formation of $Pb_2Nb_2O_7$ is recognized in PZT powders, indicating 850 °C is not high enough for PZT raw powders to

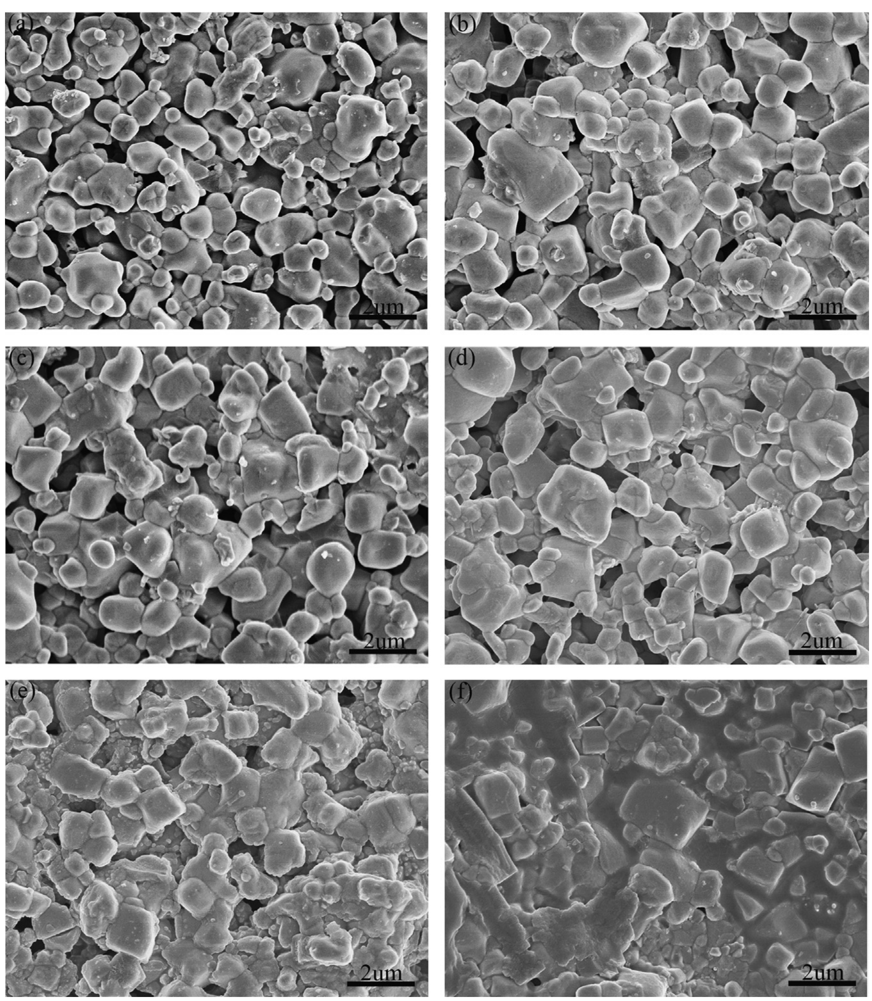


**Fig. 2.** SEM images of PZN–PNN–PZT thick films with different contents of sintering aids: (a) 0 wt%, (b) 0.5 wt%, (c) 1 wt%, (d) 1.5 wt%, (e) 2 wt%, (f) 3 wt%.