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Effects of sintering behavior on piezoelectric properties of porous PZT ceramics

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Abstract

Porous lead zirconate titanate (PZT) ceramics were fabricated by the gel-casting process of particle-stabilized wet foams and sintered at different temperatures. The bulk density and grain size of porous PZT ceramics increased with the increase of sintering temperature from 1150 to 1250 °C, which exerted remarkable influence on the value of relative permittivity (ε_r) and piezoelectric strain coefficient (d_{31} and d_{33}). The relationship between microstructure and electric properties was explained by the space-charge theory reasonably. Under the joint effects of bulk density and grain size, the value of d_h and g_h decreased with the increase of sintering temperature, resulting in the decrease of hydrostatic figure of merit (HFOM) values from 12633 to 3427×10^{-15} Pa^{-1}.

Keywords: A. Sintering; C. Dielectric properties; C. Piezoelectric properties; D. PZT

1. Introduction

Porous lead zirconate titanate (PZT) ceramics have been extensively utilized for a host of sensor and actuator applications due to their low density, improved hydrostatic figure of merit (HFOM) and coupling with biological tissue or water [1–3]. In recent years, various processing techniques have been developed to produce porous PZT ceramics, including the lost wax replication of a coral skeleton [4], mixing of burnable plastic spheres (BURPS) processes [5,6], freeze casting [7,8], and gel-casting [9–11] etc. Each process results in the formation of its own microstructure and properties with varied porosities. No matter which processing technique is employed to fabricate porous PZT ceramics, the sintering of green bodies to ceramics is traditionally an inevitable procedure. Generally, sintering is the process of joining ceramic particles together using heat without melting them. During the sintering procedure, the residual water and organics (if necessary) are removed, and the green bodies are densified with the growth of grain size. It is expected that the bulk density, microstructures such as pore size, pore morphology and grain size of ceramics can be partly tailored by adjusting the sintering behavior. As far as to the porous piezoelectric ceramics, the electric properties are closely related not only to the raw materials (PZT), but also the bulk density and structures of specimens. Therefore, it is necessary to investigate the effects of sintering behavior on the structural and electric properties of porous PZT ceramics.

Our group has successfully produced porous PZT ceramics with excellent piezoelectric properties from particle-stabilized foams via gel-casting. Comparing with the sacrificial template and TBA-based gel-casting methods etc, our technology not only possesses the advantages of simplicity, versatility and low cost, but also can fabricate porous PZT ceramics with a broad range of porosity and a high value of hydrostatic figure of merit (HFOM) [9,10]. However, we have only discussed the effects of composition of slurry on the structure and electric properties of porous PZT ceramics, further research is still needed to comprehend the technique thoroughly, such as the effects of sintering behavior on the properties of porous PZT ceramics. In this work, PZT green bodies were fabricated by combining the particle-stabilized foams and gel-casting

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technique, and sintered at different temperatures to obtain porous PZT ceramics. Then we investigated the effects of sintering behavior on the structural, dielectric and piezoelectric properties of porous PZT ceramics.

2. Experimental procedure

2.1. Materials

Commercially available PZT-5H (BaoDing HongSheng Acoustics Electron Apparatus Co. Ltd., Hebei Province, China) with a density of 7.6 g/cm^3 and a mean particle size of 1.87 μm was used as the starting material. Valeric acid ($C_5H_{10}O_2$, Sinopharm Chemical Reagent Co., Ltd., Shanghai, China) was selected as the short-chain amphiphilic molecules to hydrophobize the surface of PZT particles. A premix solution of monomers was prepared in deionized water with a concentration of 14.5 wt% of monofunctional acrylamide (AM, $C_2H_3CONH_2$) and 0.5 wt% of *N*,*N*′-methylenebisacryl amide (MBAM, $(C_2H_3CONH)_2CH_2$). Ammonium persulfate (APS, $(NH_4)_2S_2O_8$, 35 wt%) as an initiator and *N*,*N*,*N*′,*N*′-tetramethylenediamine (TEMED) as a catalyst were used for the process gelation.

2.2. Sample preparation

A slurry with an initial solid loading of 15 vol% was prepared by ball-milling quantitative PZT powder in the premix solution (water and AM monomer included) for 4 h. Afterward, an aqueous solution containing the valeric acid was slowly added to the ball-milled slurry under slight stirring to avoid local particle agglomeration. The amount of valeric acid corresponded to a concentration of 50 mmol/L in the final slurry and the pH value was fixed at 5 by employing 3 M HCl aqueous solution. Then the slurry was ball-milled again for 4 h to enable valeric acid to modify the surface of PZT particles sufficiently. The slurry foaming was carried out using a household mixer at 300 r/min for 5 min. Meanwhile, the catalyst and initiator were added to the particle-stabilized foams with the amounts of 0.5 vol% and 1 vol% respectively, and the polymerization of AM started in several minutes. The wet foams were then poured into a mold with the gelation process proceeding. After about 12 h, wet green parts were removed from molds and dried at 40 °C. The dried bodies were subsequently sintered in corundum crucibles containing $PbZrO_3$ powder to prevent lead loss with sintering temperature varying from 1150 °C to 1250 °C and holding for 2 h.

2.3. Characterization

For all tests, 3–4 samples were prepared for each experimental condition to obtain a reliable analysis. All samples were machined to be disc-shaped with 10 mm in diameter and 1.5 mm in height. The density and porosity of sintered samples were measured by using the water displacement method based on the Archimedean principles. The microstructures of porous PZT ceramics were observed by scanning electron microscopy (SEM; SSX-500, Shimazu Corp., Japan). Grain size was measured from the obtained SEM photographs using the image analysis software (Image J) [12]. For the measurement of dielectric and piezoelectric properties, both surfaces of the samples were coated with Ag paste and heated at 550 °C for 20 min to form electrodes. Subsequently, the samples were poled in a silicone oil bath at 120 °C by applying a dc field of 10 kV/cm for 25 min, and aged for 24 h before testing. The piezoelectric coefficient (d_{33}) was measured by a piezo-meter system (ZJ-3A, Institute of Acoustics, Chinese Academy of Science, China). Spectrum characteristics (f_r, the resonant vibration frequency and f_a, the anti-resonant vibration frequency) and relative permittivity (ε_r) were measured by using an impedance bridge (HP-4194A, Hewlett-Packard Development Company, CA). The transverse piezoelectric strain coefficient (d_{31}) was calculated from the formulae proposed by Yang [13]. The magnitude of HFOM was calculated from the measured values and other physical parameters such as density and diameter.

3. Results and discussion

3.1. Sintering procedure and phase analysis

As can be seen from Fig. 1, the sintering procedure of PZT porous ceramics began with an initial heating rate of 0.5 °C/min up to 120 °C, then the samples were kept at 120 °C for 1 h to remove crystal-water. Afterwards, the sintering process continued with 1 °C/min up to 500 °C and held for 3 h to assure complete removal of organics. The compacts were finally heated to sintering temperature with 1.5 °C/min and sintered at 1150, 1175, 1200, 1225 and 1250 °C for 2 h respectively, followed by furnace cooling to room temperature.

Fig. 2 shows the typical XRD patterns of PZT ceramics sintered at 1150 °C. All the peaks characterizing perovskite phase were detected in Fig. 2, which indicated the complete formation of PZT ceramics. Therefore, the sintering procedure of porous PZT ceramics employed for this research is considered to be appropriate.

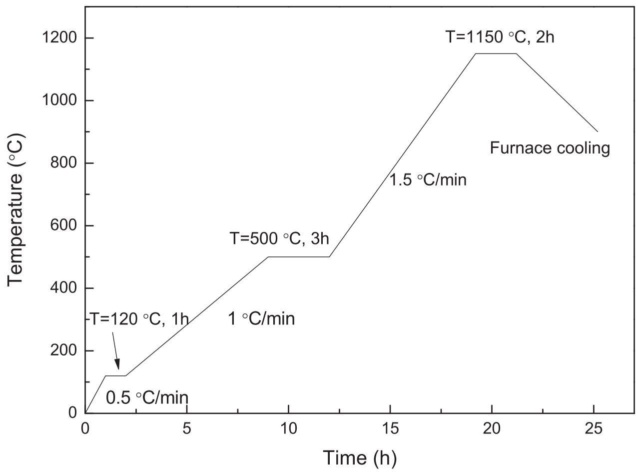

Fig. 1. Sintering procedure of porous PZT ceramics.

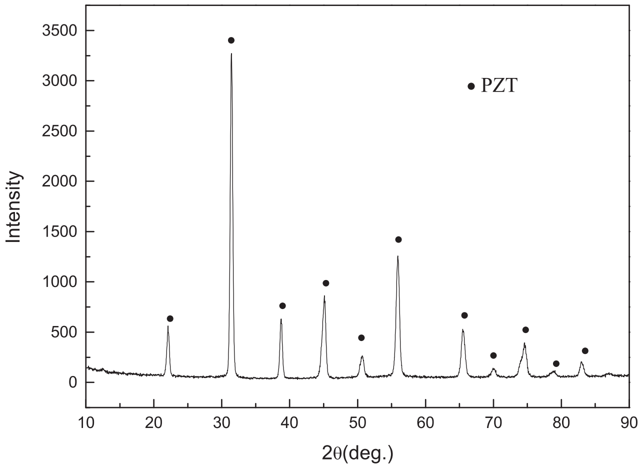

Fig. 2. XRD patterns of sintered porous ceramics.

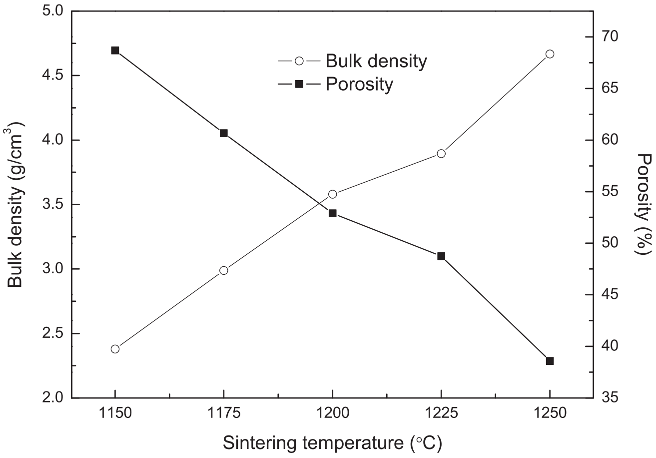

Fig. 3. Bulk density and porosity of porous PZT ceramics as a function of sintering temperature.

3.2. Porosity and microstructure

Fig. 3 shows a plot of porosity and bulk density versus sintering temperature for porous PZT ceramics. It was found that the bulk density increased from 2.38 g/cm^3 at 1150 °C to 4.67 g/cm^3 at 1250 °C, while the porosity demonstrated a declining trend from 68.70% (sintered at 1150 °C) to 38.58% (sintered at 1250 °C). Apparently, the results have revealed a broader range of density or porosity than previous research [14], which provides extensive selections for applications in underwater transducers or biomedical imaging etc.

Fig. 4 shows the detailed pore morphology and interconnection of sintered porous ceramics with different sintering temperatures. As can be seen from Fig. 4(a), macropores with the pore size ranging from 120 μm to 350 μm were formed in the porous PZT ceramics, and interconnected structure of open-cells were resembled. While concerning on the interconnection of particles, it was observed from Fig. 4(b)–(f), with the sintering temperature increasing from 1150 °C to 1250 °C, the particles got closer to each other and the open pores disappeared gradually. Meanwhile, the average grain size grew up from 1.25 μm to 5.93 μm with small grains merging into larger ones.

3.3. Dielectric and piezoelectric properties

Fig. 5 shows the relative permittivity (ε_r) of porous PZT ceramics measured at different frequencies. For all investigated specimens, the relative permittivity decreased with increasing frequency, which is consistent with general ferroelectrics. While settling at a fixed frequency, the relative permittivity increased with the increase of sintering temperature or the corresponding decrease of porosity, which is mainly due to the exclusion of air that possessed lower permittivity than PZT phase. Besides, the values of relative permittivity measured at 1 kHz ranged from 390.4 to 951.6, much higher than that of our previous specimens with similar porosities [9,10]. As discussed above, the grain size increased obviously with the increase of sintering temperature, resulting in the decrease of grain boundary with relatively low permittivity than PZT grains, so the relative permittivity of samples increased with sintering temperatures remarkably than that of previous researches.

As can be seen from Fig. 6, the d_{33} and d_{31} values of porous PZT ceramics increased almost linearly with an increase of sintering temperature, which was caused jointly by the increase of bulk density and grain size together. Firstly, as the bulk density increased from 2.38 to 4.67 g/cm^3, the gradual elimination of air which exhibits low piezoelectric coefficient led to the increase of d_{33} and d_{31} values. Moreover, according to the observation from Okazaki and Nagata [15], the space-charge sites such as lattice vacancies and impurity atoms inside grain boundaries and domain walls often create the space-charge field and restrict the movement of domain walls. When the average grain size of porous PZT ceramics grew up from 2.19 μm to 5.93 μm with sintering temperature, the surface area of the space-charge field decreased accordingly, which reduced the impeditive effects on the movement of domain walls and improved the piezoelectric coefficients obviously. Meanwhile, it is important to note that the faster ascending trend of d_{31} value than that of d_{33} would definitely lead to the decrease of d_h ($=d_{33}+2d_{31}$) with sintering temperature.

The hydrostatic voltage coefficient (g_h) can be calculated from the following formula:

$$g_h = d_h/\varepsilon_r\varepsilon_0 \tag{1}$$

where ε_0 is the permittivity of the air. As shown in Fig. 7, the g_h values decreased from 60.5 to 20.2×10^{-3} Vm/N with the sintering temperature, which was mainly due to the decrease of d_h value and the increase of ε_r value of the porous PZT ceramics.

Fig. 8 shows the effects of sintering temperature on the variation in hydrostatic figure of merit (HFOM$=d_h \times g_h$). As sintering temperature increased, the HFOM values decreased from 12633 to 3427×10^{-15} Pa^{-1}. The changing trend of HFOM values in this research is completely opposite to that of previous literature proposed by Zeng et al. [16]. The reason for this could be explained as follows: first, with the

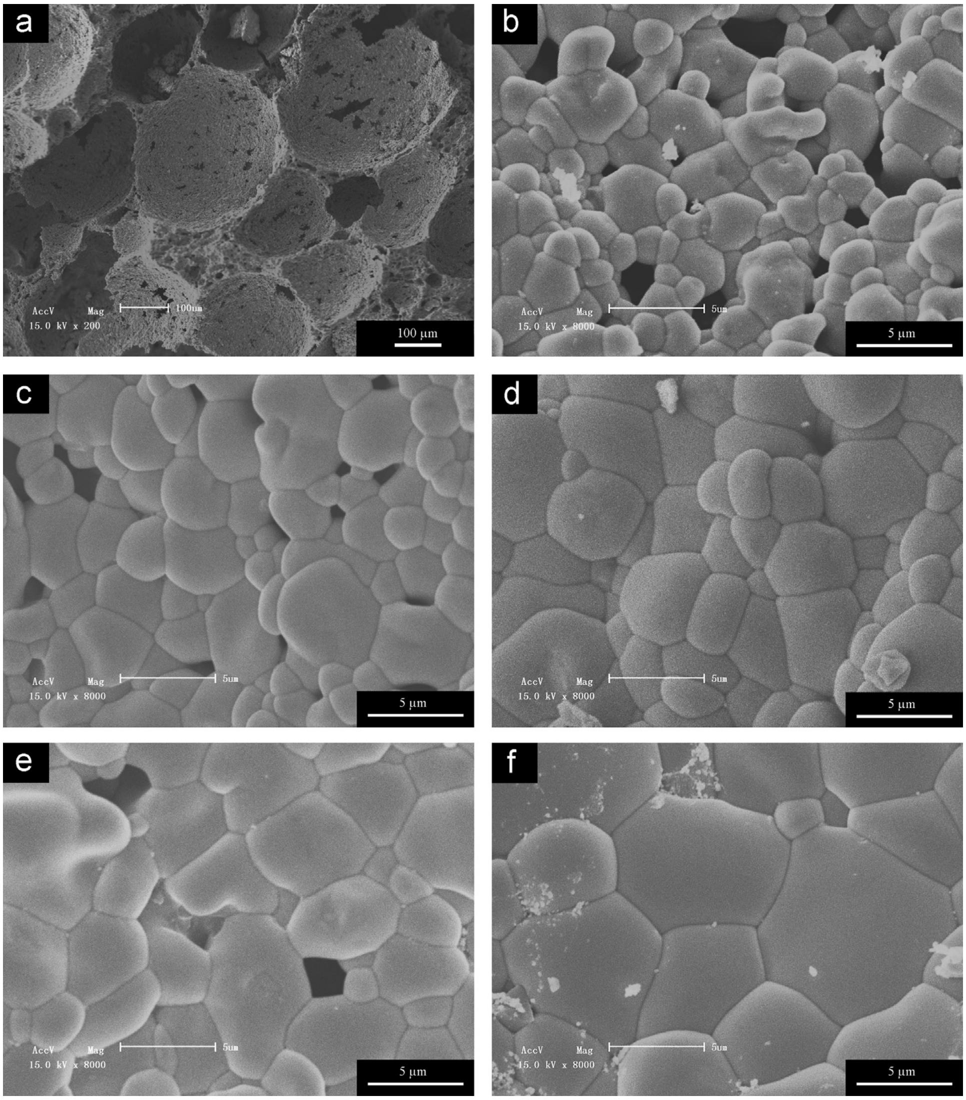

Fig. 4. Pore morphology of porous PZT ceramics sintered at different temperatures: (a) 1150 °C, at low magnification; (b) 1150 °C; (c) 1175 °C; (d) 1200 °C; (e) 1225 °C and (f) 1250 °C.

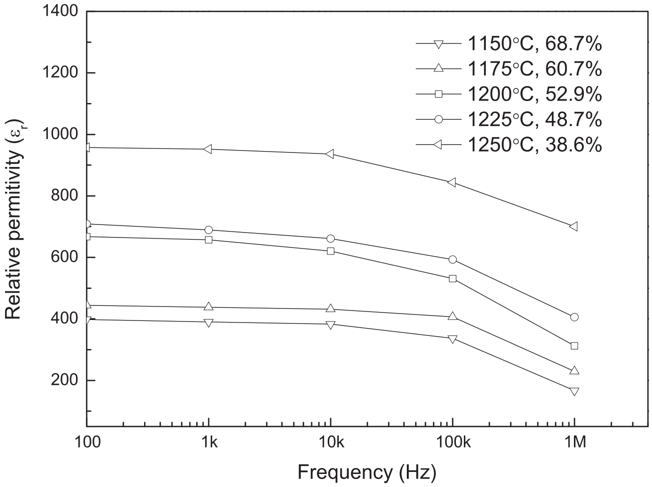

Fig. 5. Variations of relative permittivity with frequency for samples sintered at different temperatures.

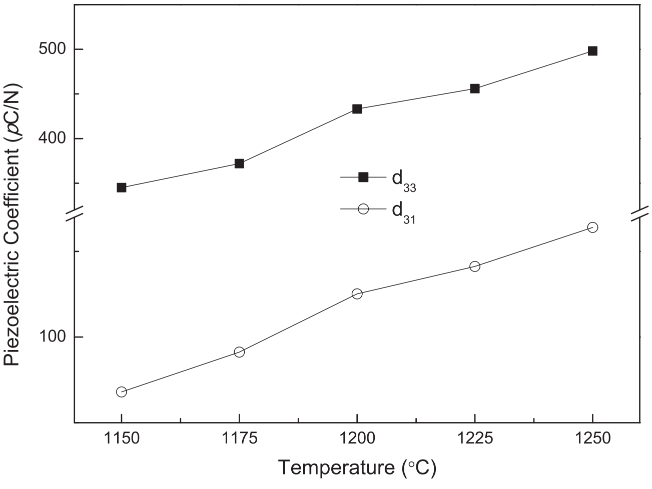

Fig. 6. Longitudinal piezoelectric strain coefficient (d_{33}) and transverse piezoelectric strain coefficient (d_{31}) values of porous PZT ceramics sintered at different temperatures.

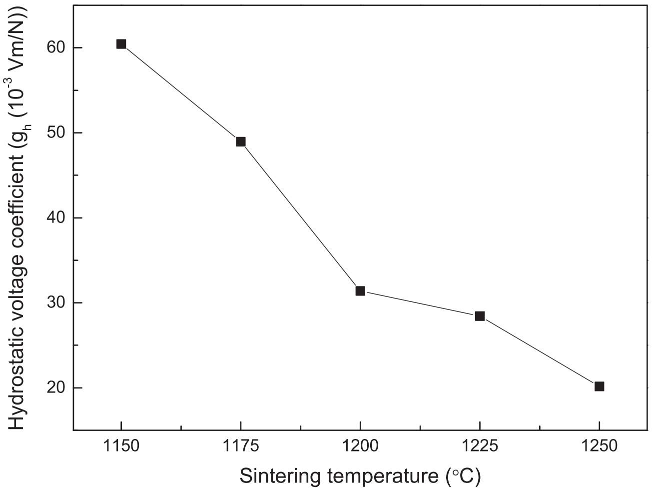

Fig. 7. Hydrostatic voltage coefficient (g_h) values of porous PZT ceramics sintered at different temperatures.

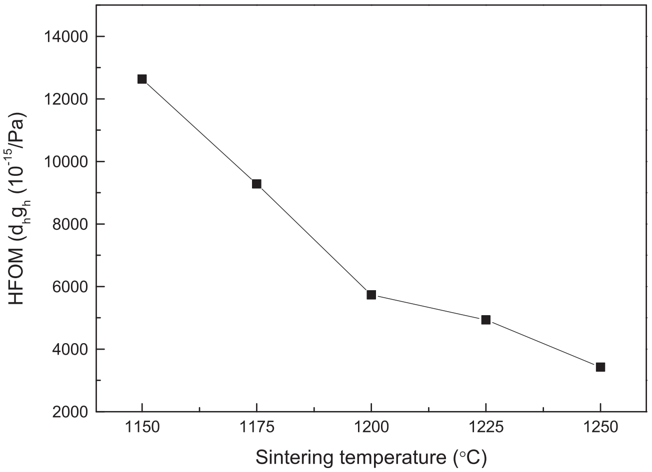

Fig. 8. Hydrostatic figure of merit (HFOM) of porous PZT ceramics sintered at different temperatures.

increase of sintering temperature, the rapid increasing trend of d_{31} value than d_{33} and the opposite sign of the two parameters made the value of d_h decrease obviously, which exhibited a different changing trend with Zeng′s and our previous research [9,10,16]. Therefore, with respect to the value of piezoelectric strain coefficient (d_{33}, d_{31}), the grain size served as a prevailing influencing factor than bulk density in this research. Meanwhile, the decrease of g_h also induced the decline of HFOM values. As a result, the changing trend of HFOM with the sintering temperature was opposite to Zeng′s research.

4. Conclusion

In this work, porous PZT ceramics were prepared from particle-stabilized foams via gel-casting technique and sintered at different temperatures. While sintering temperature increased from 1150 to 1250 °C, the bulk density and grain size of porous PZT ceramics increased obviously. As far as the dielectric and piezoelectric properties, the value of ε_r, d_{31} and d_{33} of porous PZT ceramics not only increased with increasing bulk density, but also were affected by the grain size, which can be explained by the space-charge theory. The value of d_h and g_h decreased with the increase of sintering temperature, which led to the decrease of HFOM values. As a result, the value of HFOM was maximized at the temperature of 1150 °C, while the relative permittivity, which was related to the stability and reliability of specimen, was at its lowest value. Therefore, a compromise should be made while selecting the sintering temperature to achieve appropriate values of HFOM and relative permittivity simultaneously.

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