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Effects of sintering behavior on microstructure and piezoelectric properties of porous PZT ceramics

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Abstract

Porous lead zirconate titanate (PZT) ceramics with interconnected pores were fabricated by using a novel tert-butyl alcohol (TBA)-based gel-casting method. The resultant samples were sintered at different temperatures and subsequently characterized in terms of both microstructure and piezoelectric properties to study effects of sintering behavior. Both microstructure and piezoelectric properties exhibited obvious dependence on sintering temperature. It was noted that porosity and grain size played dominant roles in determining the magnitudes of dielectric constant (ε) and piezoelectric constant d_{33}, respectively. With the increase of sintering temperature, the porosity declined and the grain size increased which exerted opposite influences on piezoelectric properties mainly via ε and d_{33}. Since anti-interference ability of the ceramic correlates linearly with ε, it is possible to adjust sintering temperature to tailor porosity and pore morphology in order to achieve optimum piezoelectric properties as well as relatively high anti-interference ability.

Keywords: A. Sintering; B. Porosity; C. Piezoelectric properties; D. PZT

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1. Introduction

Porous PZT ceramics have been of great interest and technological importance in ultrasonic applications such as hydrophones, actuators and underwater transducers [1–3]. This results from their ability to accomplish coupling between mechanical and electric signals as well as their possibility of obtaining very high values for some piezoelectric coefficients compared with dense materials. Intense attention has been attached to the study of porous PZT ceramics mainly for the following several reasons. First, since piezoelectric coefficients d_{33} and d_{31} are opposite in sign, hydrostatic piezoelectric strain coefficient, d_h ($=d_{33}+2d_{31}$), has a small value. Previous research [4,5] has demonstrated that increasing porosity can result in moderate decline in d_{33} but rapid reduction in d_{31}, contributing to the value of d_h. Second, inclusion of air phase reduces dielectric constant (ε) of the bodies considerably, leading to increase in hydrostatic piezoelectric voltage coefficient g_h, which can be calculated by d_h/ε. Thus, hydrostatic figure of merit (HFOM, $d_h \cdot g_h$), defined to evaluate the overall performance of a piezoelectric ceramic used as a hydrophone, can be significantly improved. Third, porous PZT ceramics provide a solution to the problem of poor acoustic matching between ceramics and media for their low density. In short, porous PZT ceramics have emerged as a promising candidate over dense materials in many applications. Consequently, a large amount of research has been carried out involving various manufacturing techniques to produce porous PZT ceramics [6–8] and parameters possibly influencing their properties [9–12]. The key problems in this area mainly involve the conflicts between desired porosity and mechanical strength, piezoelectric properties and anti-interference ability. Although almost all manufacturing techniques have their own limitations or drawbacks, they offer alternative perspectives to the acquisition of porous PZT ceramics with certain merits. In addition, the sintering behavior, which relates directly to the microstructure of pores and exerts significant influence on the final piezoelectric properties, lacks sufficient investigation. Therefore, the aim of this paper is to fabricate porous PZT ceramics with high strength by using a novel tert-butyl alcohol (TBA)-based gel-casting method. Furthermore, it is the aim to characterize the sintered ceramics in terms of both micro-

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structure and piezoelectric properties to study the effects of sintering behavior.

2. Experiment procedure

2.1. Materials

The starting materials were commercially available PZT-5H with a mean particle size of 1.866 μm and a density of 7.6 g/cm^3. Tert-butyl alcohol (TBA, chemical purity, Beijing Yili Chemical Co., China) was used as shaping solvent. A premix solution was prepared by adding into TBA acrylamide (AM, $C_2H_3CONH_2$) and N,N′-methylenebisacrylamide (MBAM, $(C_2H_3CONH)_2CH_2$) with concentrations of 14.5 wt% and 0.5 wt%, respectively. Ammonium persulfate (APS, $(NH_4)_2S_2O_8$), 40 wt%) as initiator and N,N,N,N-tetramethylethylenediamine (TEMED, 20 wt%) as catalyst were employed in the gelation process.

2.2. Sample preparation

Preparing a liquid suspension (slurry), molding, drying, binder removal and subsequent sintering of green bodies constitute a typical process of the sample preparation in TBA-based gel-casting method. A slurry containing PZT powder (solid loading 15 vol%) and the premix solution (TBA and AM monomer included) was prepared by ball milling the mixture for 5–6 h. After initiator and catalyst with appropriate amounts were added to the slurry while stirring, the gelation process was started and the polymerization of AM occurred in several minutes. The slurry was then poured into molds while in situ polymerization continued at around room temperature. After about 1 h, green bodies were removed from molds and dried at 50 °C. TBA evaporated smoothly leaving pores behind in the bodies. The dried samples, which had no obvious shrinkage in the above drying process, were then sintered in a crucible under a lead oxide atmosphere to prevent lead loss with sintering temperature varying from 1150 °C to 1250 °C and holding for 2 h.

2.3. Characterization

After fabricated, all samples were machined to be disc-shaped with a typical size of 10 mm in diameter and 1.5 mm in height. The bulk density of the sintered samples was measured from sample mass and dimension, and the relative density thus porosity were obtained from the ratio of the measured bulk density to the theoretical one of this PZT material, which was taken as 7.6 g/cm^3. The samples were analyzed by X-ray diffraction (SHIMAZU S-7000) to reveal the phases of the powder and sintered ceramics. The microstructure of the porous PZT ceramics was observed by a SSX-550 scanning electron microscope (SHIMAZU). To evaluate the dielectric and piezoelectric properties, electrodes were made by carefully pasting a thin silver layer to both surfaces of the samples, followed by heat treatment at around 500 °C for 20 min. Thereafter, the samples were poled at 120 °C for 15 min under a DC electric field of 2 kV/mm in a bath of silicone oil, and were subsequently aged for 24 h before testing. The piezoelectric constant (d_{33}) was measured by a Quastic-static d_{33}-meter (ZJ-3A). Frequency spectrum characteristics and dielectric constant were measured by using an impedance bridge (HP-4194A). The magnitude of HFOM was calculated from the measured values and other physical parameters such as density and diameter.

3. Results and discussion

The samples obtained in this study are summarized in Table 1 (the quoted data in this table were measured and calculated from 3 to 4 samples in one batch under each experimental condition). The quoted grain sizes were measured from scanning electron microscope, using the line intersection method.

3.1. Determination of sintering procedure

Appropriate sintering procedure is of great importance because the samples are easy to crack in the sintering process due to high porosity and other possible defects. To preserve the interconnections between grains while ensuring full sintering of the samples, sintering procedure was determined by the thermo-gravimetric analysis of the green body shown in Fig. 1(a). It was observed that the organic phases were completely burned out after 600 °C. It was also noted that there were two exothermic peaks at about 350 °C and 440 °C indicating intense degradation of the organic phase. The polymer decomposed to small molecules and most of these small molecules burned off at the first exothermic temperature while the residual molecules burned off later creating a second exothermic peak. Therefore, an optimum heating procedure began with an initial heating rate of 120 °C/h up to 350 °C followed by 60 °C/h up to 450 °C and finally 120 °C/h up to 700 °C to assure complete burn out of the

Table 1
Summary of the samples prepared in this study.

Sample group	Sintering temperature (°C)	Linear shrinkage (%)	Porosity (%)	Grain size (μm)	Relative dielectric constant (ε_r)	d_{33} (pC/N)	$d_h \cdot g_h$ (10^{-15} m^2/N)
A	1150	15.1	57.6	1.74	502	454	22299
B	1175	23.6	49.5	2.06	905	492	19071
C	1200	27.8	45.3	2.73	1187	498	11723
D	1225	30.9	37.9	3.29	1636	568	7607
E	1250	34.2	23.9	3.58	2513	588	5964

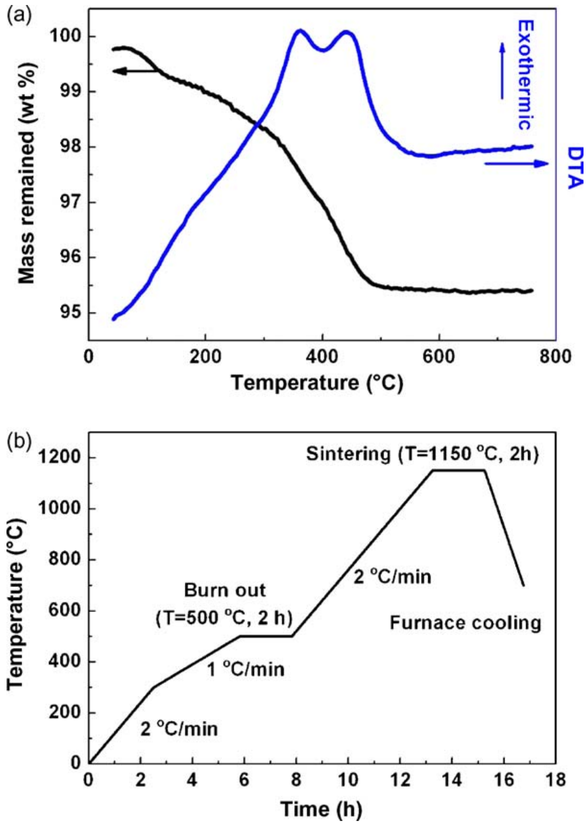

Fig. 1. (a) Thermal analysis results of the green body as a function of the temperature at a heating rate of 10 °C/min in air, and (b) a typical sintering procedure.

organics. The samples were subsequently sintered at 1150–1250 °C with 25 °C interval for 2 h. A typical sintering procedure is illustrated in Fig. 1(b).

Fig. 2 reveals typical XRD patterns of PZT powder and sintered porous ceramics. It could be observed that perovskite structure was exhibited for both the calcined powder and sintered ceramics with no other phase detected indicating that the powder and sintering procedure employed in the present work were appropriate.

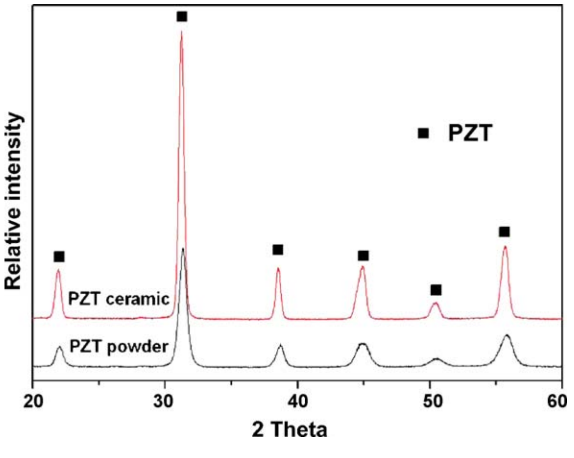

Fig. 2. Typical XRD patterns of PZT powder and sintered porous ceramics.

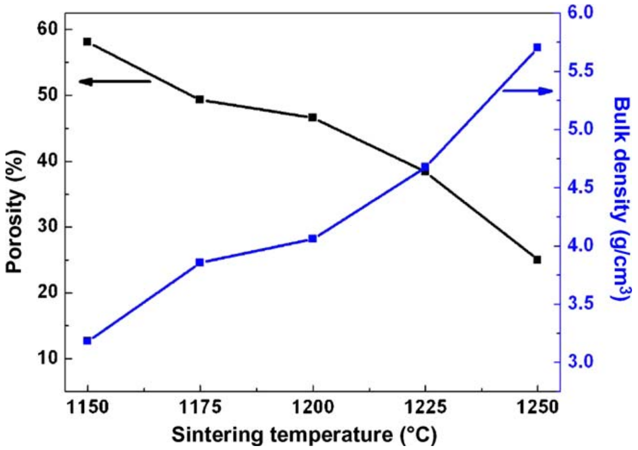

Fig. 3. Change in porosity and bulk density as functions of sintering temperature.

3.2. Porosity and pore morphology

Fig. 3 shows the changes of porosity and bulk density with the increase of sintering temperature. The porosity decreased as the sintering temperature increased due to the process of sintering densification. Meanwhile, the bulk density of the body increased towards that of dense materials. The density of a piezoelectric ceramic used for a hydrophone or transducer was very important in that efficient energy transfer could be achieved only through excellent impedance matching. The detailed pore morphology and interconnection in the sintered ceramics are shown in Fig. 4. From these SEM micrographs, it could be observed that the grains grew up and the porosity decreased as the sintering temperature increased from 1150 °C to 1250 °C. These change trends could be verified by the measured values of grain size and porosity presented in Table 1. Furthermore, with the increase of the sintering temperature, there was a tendency for small grains to be even smaller and large grains to be even larger. In addition, all samples had homogeneous pore distribution and 3–3 connection structure with pore size around several microns. Fig. 4(f) shows the typical connection of grains from which the sintering neck and the local structure similar to stone arch bridges can be easily observed. These unique structures made it possible for the bodies to obtain high mechanical strength, easy to handle during the fabrication process and more adaptive to the working condition.

3.3. Dielectric and piezoelectric properties

With the increase of sintering temperature, the bulk density of the samples increased approaching that of dense materials which could be inferred from Fig. 3. Therefore, the relative dielectric constant of the samples, measured at 1 kHz as shown in Fig. 5, increased due to the increase in proportion of active piezoelectric ceramic phase and the dominating effects of it over passive phase (air). The result was easily understood and consistent with former research [7,13].

Fig. 6 shows the change of piezoelectric constant d_{33} and HFOM with sintering temperature. According to the study of Okazaki and Nagata [9], there are certain space-charge sites

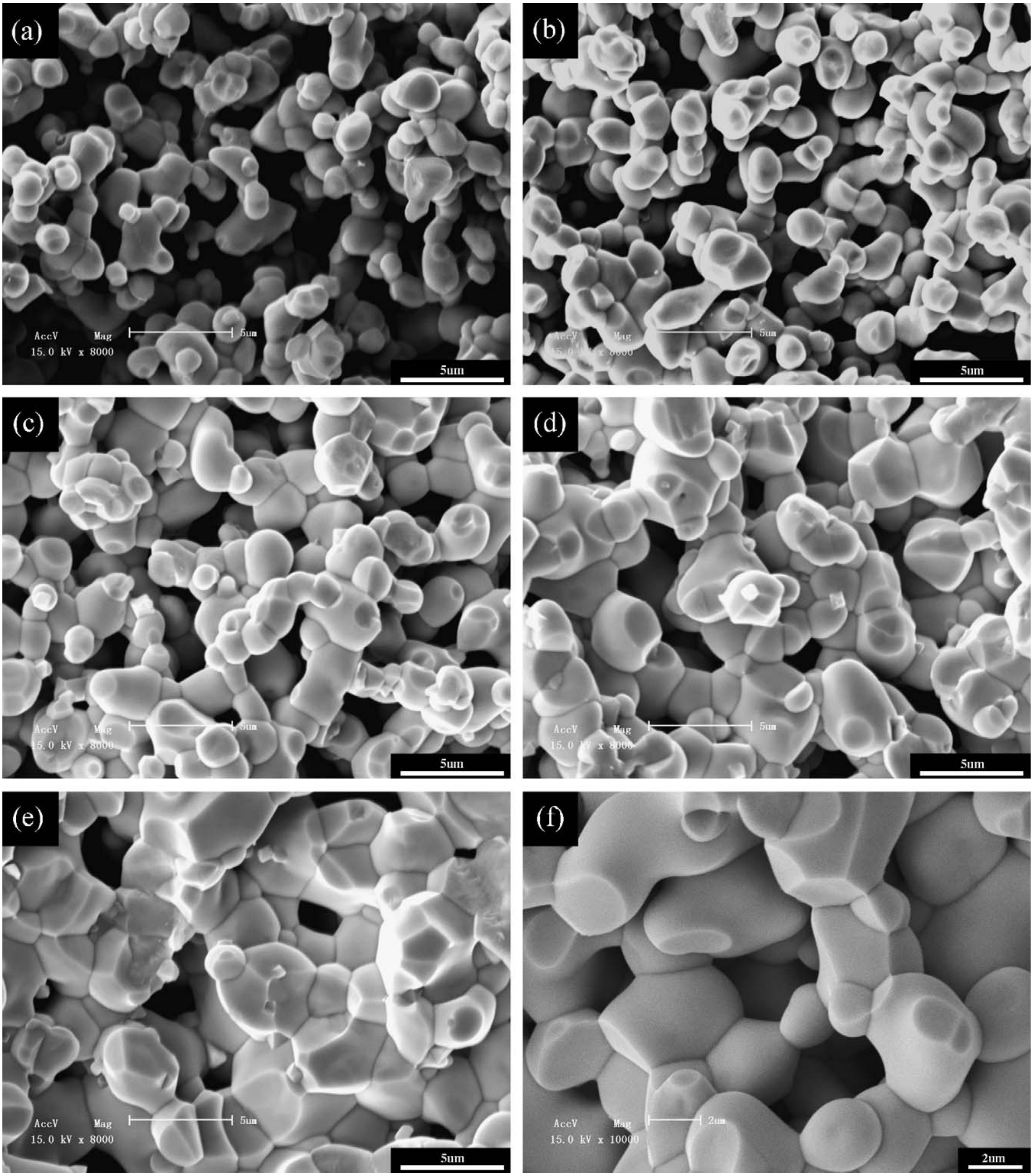

Fig. 4. Pore morphology and network structure of sintered porous PZT ceramics: (a) 1150 °C, (b) 1175 °C, (c) 1200 °C, (d) 1225 °C, (e) 1250 °C and (f) typical connection of grains.

inside grain boundaries and domain walls such as impurity atoms and lattice vacancies creating a space-charge field to restrict the movement of domain walls. As the grain size increased, the surface area of the space-charge field which impeded the movement of domain walls decreased significantly thus piezoelectric coefficients could be improved. Similarly, previous research has also demonstrated that piezoelectric parameters have always shown an increase with increasing grain size [10] because the domain walls are expected to be quite free in larger grains considering that grain boundaries will contribute additional pinning points to the moving walls. Meanwhile, the increase trend of d_{33} with sintering temperature can be explained by considering gradual elimination of air phase which has little contribution to the piezoelectric effect.

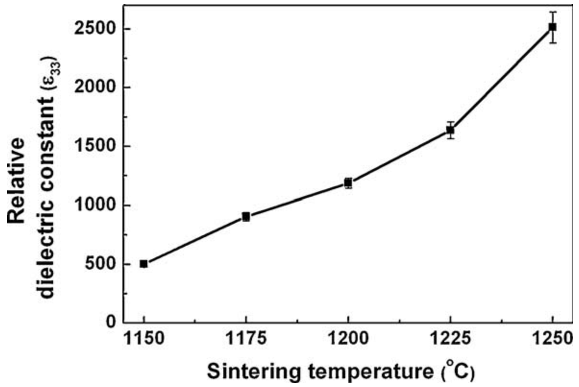

Fig. 5. Relative dielectric constant as a function of sintering temperature.

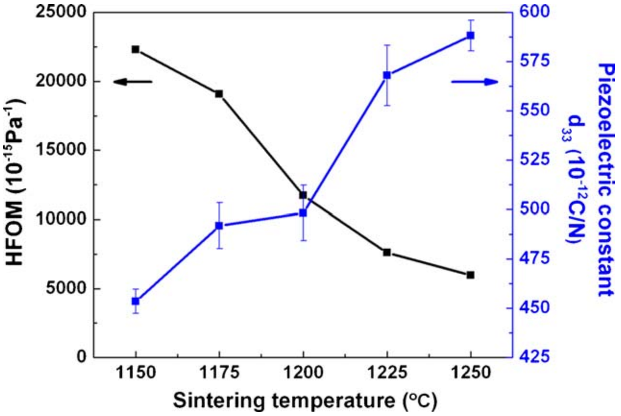

Fig. 6. Change of piezoelectric constant d_{33} and HFOM with sintering temperature.

However, the study of Okazaki and Nagata [9] also shows that the piezoelectric constants are affected more markedly by the grain size than by the porosity. Therefore, as for the value of d_{33}, the grain size, affected by sintering temperature, served as a dominant influencing factor.

As sintering temperature increased, although the value of d_{33} approached that of dense materials, the rapid increase in relative dielectric constant led to severe decline of g_{h} and hence the value of HFOM shown in Fig. 6. To evaluate the effects of sintering temperature on the value of HFOM, two parameters, i.e. porosity and grain size should be taken into consideration at the same time. With the increase of sintering temperature, on one hand, the grain size increased leading to increase of d_{33} and contributing to the value of HFOM; on the other hand, the relative dielectric constant increased rapidly due to the decrease of porosity, undermining the value of HFOM. Obviously the latter effect prevailed over the former one in this study leading to the decrease of HFOM. The dominant role of porosity in determining the value of relative dielectric constant and the dominating effects of grain size in determining d_{33} agreeing with the ideas in former results discussed above can fairly explain the result of this study. It was worth mentioning that the values of HFOM of the sintered ceramics were unexceptionally extremely high compared with that of dense materials (80×10^{-15} Pa^{-1}), especially the ones sintered at 1150 °C.

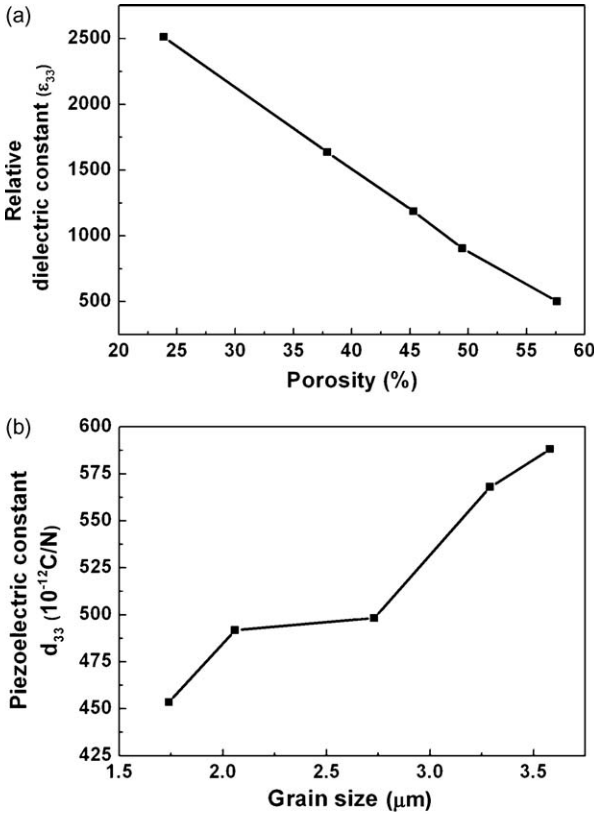

Fig. 7. (a) Relative dielectric constant as a function of porosity and (b) piezoelectric constant d_{33} as a function of grain size.

To evaluate the effects of porosity and grain size on relative dielectric constant and piezoelectric constant d_{33}, Fig. 7 illustrates the relationship. Fig. 7(a) shows an approximately linear dependence of relative dielectric constant on porosity while in Fig. 7(b), the correlation of d_{33}-grain size is exactly the same with that of d_{33}-sintering temperature. These figures attested to the primary dependence to a certain extent. Admittedly, detailed relationship of these two pairs, i.e., dependence of d_{33} on grain size and relative dielectric constant on porosity, should be further investigated by firstly ruling out the influence of each other. It has been an effective attempt to control grain size and porosity respectively to examine and demonstrate the underlying effects [9].

It was noted in this study that the sintering temperature 1150 °C was enough for full sintering of the samples. Consequently, the value of HFOM could be maximized at this temperature according to the result. However, the relative dielectric constant, which was proportionally related to the anti-interference ability of the samples, was at its lowest value at this temperature. Therefore, a compromise should be made when deciding the sintering temperature to achieve optimum values of piezoelectric properties and relative dielectric constant simultaneously.

4. Conclusion

Porous PZT ceramics were prepared by using a novel TBA-based gel-casting method and sintered at different temperatures. It was found that sintering behavior had obvious effects on the microstructure and piezoelectric properties. With the increase of sintering temperature, the microstructure of the samples changed accordingly and the porosity decreased which led to increase in relative dielectric constant hence lowered HFOM. Furthermore, the grain size increased with sintering temperature contributing to the value of piezoelectric properties such as d_{33} and HFOM. It could be inferred that the porosity played a dominant role in determining the value of HFOM in this study. As a result, it is practical and feasible to adjust sintering temperature to tailor porosity, pore morphology and hence piezoelectric properties as well as ensuring relatively high anti-interference ability of the samples.

Acknowledgements

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