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Properties of Nb doped Zr-rich PZT ceramics prepared by a heterogenous precipitation method

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Abstract A novel heterogenous precipitation method (H-P) combining the merits of solid state synthesis method (S-S-S) and the liquid routes was developed to synthesize the ZrO_2 phase-free Zr-rich $Pb_{0.99}Nb_{0.02}(Zr_{0.965}Ti_{0.035})O_3$ ceramics. The microstructure of the ceramics synthesized by H-P was more homogeneous and fine than that by S-S-S. The density, the dissipation factor, the ferroelectric properties and the dielectric breakdown of the ceramics synthesized by H-P are more outstanding than that by S-S-S. The dielectric breakdown (E_b) increases markedly from 5 kV/mm to 6.5 kV/mm.

Introduction

Solid solutions Lead Zirconate Titanate, ($Pb(Zr_xTi_{1-x})O_3$, PZT), and related ceramics are known as some of the most useful piezoelectric, ferroelectric and pyroelectric materials, which have found widespread applications in pressure sensors, ultrasonic motors, transducers, stack-type actuators and pyroelectric detector[1–3]. In the Zr-rich PZT ceramics there exits a ferroelectric (FE) and anti-ferroelectric (AFE) phase boundary for a Zr/Ti ratio = 95/5 [4, 5]. In a certain range near the FE and AFE phase boundary, the FE phase and the AFE phase can co-exist. This kind of Zr-rich PZT ceramics has gained technical applications for its high-density energy storage and its high-density power output [6–11]. Nevertheless, the relative low E_b and reliability are still a great disadvantage for its applications. In particular, for further high-power applications, such as, electron source for high power microwave generation and ferroelectric electron emission, the E_b of PZT material is also a absolute key to determine their emission ability [12]. Since copious electron emission from a PZT ferroelectric was firstly reported by Miller and Savage in 1959 [13], Many research jobs have proved that there exits a threshold value named the trigger voltage, below which no emission is observed and the peak value of the beam current increases with the increase of the trigger voltage. The fact of relative low E_b of PZT ferroelectric cathode has become a critical limitation on their ability to emit electrons. Because both uniform microstructures and high density are important to ceramics with the controlled microstructure and high E_b [14,18].Therefore, the present trend is to make such materials and devices in a smaller size, which requires fine grain ceramics with uniform microstructures and high density.

In S-S-S method, Lead Titanate is the first reaction product to appear before the PZT solid solution is formed because of the higher diffusion coefficients of Pb^{2+} and Ti^{4+} compared Zr^{4+} [15]. Therefore, PZT grains show a gradient of Zr/Ti concentration from the core to the shell in the process of formation of perovskite phase and the properties of materials are sensitive to the Zr/Ti [15, 16]. It is not easy for S-S-S method to reach the homogenous distribution of Ti^{4+}

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only by solid state grinding process. Besides, solid state synthesis always require high processing temperatures and also induce impurities during ball milling process and such mixing procedure cannot lead to ideal compositional and structural homogeneities in ceramics produced. Compared to S-S-S method, powders prepared by hydroxide coprecipitation are more homogeneous and reactive. However, almost every wet chemistry-based processing routes require the precursor powders to be calcined in a temperature range of 600–900 °C in order to develop the designed PZT phase. This often results in particle agglomerates in the resulting powder. The presence of these hard particle agglomerates will significantly reduce the sinterability of the powder compact and lead to microstructural defects in the sintered PZT ceramics [18]. The powders prepared by the sol-gel process are more homogeneous and fine. However, the output of sol–gel process is too small and the cost of sol–gel process is higher than the other methods, which is an obvious drawback for mass production [19]. So a novel H-P method combining the merits of S-S-S and the liquid route was developed. The objective of the present work is to investigate the effect of different powder processing routes on the microstructure and the properties of PZT ceramics by comparing the S-S-S method with the H-P method. The composition of material is $Pb_{0.99}Nb_{0.02}(Zr_{0.965}Ti_{0.035})O_3$, the aim of adding small amounts of Nb_2O_5 as soft dopant is to decrease the coercive field and increase the electromechanical coupling factor and volume resistivity [20].

Experiments

Starting materials used in this study were Nb_2O_5(purity 99.99%, Shanghai Yuelong Chemical Plant, China), NH_4OH(purity 21–22% NH_3,Shanghai No.4 Reagent & H.V. Chemical Co., Ltd, China), Pb_3O_4(purity 97.33%, Shanghai Longrun Chemical Plant, China), TiO_2(purity 98.42%, Shanghai Hengxin Reagent Co., Ltd, China), ZrO_2(purity 99.09%, Jieshui Reagent Co., Ltd, Jiangxi Province, China), $Ti(SO_4)_2$(purity 96%, Nanhuipengyingzhen Chemical Plant, China). For preparing $TiO(NO_3)_2$ solution, $Ti(SO_4)_2$ was dissolved in aqueous solution and precipitated by NH_4OH. After washed with water for several times, $Ti(OH)_4$ precipitate was reacted by HNO_3 to form a 0.1 mol.dm^{-3} $TiO(NO_3)_2$ solution. The reaction is shown in the following equation:

$$Ti(SO_4)_2 + 4(NH_4OH) \rightleftharpoons Ti(OH)_4 \downarrow + 2(HN_4)_2SO_4 \quad (1)$$

$$Ti(OH)_4 + 2HNO_3 \rightleftharpoons TiO(NO_3)_2 + 2H_2O \quad (2)$$

The detailed scheme of the H-P method process is given in Fig. 1. The three starting solid powders ZrO_2, Pb_3O_4, Nb_2O_5 and liquid $TiO(NO_3)_2$ were mixed in a polyethylene pot for 12 h using distilled water and ZrO_2 balls as the grinding medium. Then NH_4OH solution of 1 M was added to the homogeneous slurry obtained above under vigorous stirring. The $TiO(NO_3)_2$ formed $Ti(OH)_4$ precipitate, which dispersed homogeneously in the slurry. The corresponding equation is:

$$\begin{aligned} &TiO(NO_3)_2 + 4NH_4OH \\ &\rightleftharpoons Ti(OH)_4 \downarrow 2NH_4NO_3 + 2NH_3 \uparrow + H_2O \end{aligned} \quad (3)$$

In order to ensure the reaction, an excess of NH_4OH was added in the slurry and pH value of mixture was 9–10 [17]. The dried powder was calcined at 550 °C to decompose the $Ti(OH)_4$ precipitate into TiO_2[18]. The calcined powder was ball-milled for 24 h again. After drying, the powders were pressed into discs (Φ15 mm × 2 mm) .The materials were sintered at different temperatures (1260–1360 °C) for about 1.5 h in an atmosphere controlled by the same sintered ceramic powder in double high-purity-alumina crucibles. A powder and ceramics of $Pb_{0.99}Nb_{0.02}(Zr_{0.965}Ti_{0.035})O_3$ was also prepared by the S-S-S method, which experienced a synthesis process at 850 °C and an excess of 1 wt% PbO in the starting raw powders according to our experience in evaporation of PbO in S-S-S method, see in Fig. 1.

X-ray diffraction (XRD) pattern was obtained using an automated diffractometer (Model Rigaku RAX-10) with Cu Kα1 radiation. The microstructure of the sintered ceramics was analyzed by field emission scanning electron microscope (FESEM) (JSM-6700F, JEOL, Japan). A transmission electron microscope (TEM) with energy dispersive spectroscope (EDS) (Model JEM-200CX) was applied to investigate the microstructure of the powders. The density of the sintered bodies was determined by the Archimedes method. For electrical measurements, Ag-paste was pasted on both sides of the discs and then fired at 650 °C for 30 min. The electroded specimens were poled in silicone oil at 120 °C by applying a dc field of 2.5 kV/mm for 20 min. The piezoelectric constant was measured using a d_{33} meter (Model ZJ-3D, Institute of Acoustics, Beijing, China). The dielectric constants and dielectric loss at 1 kHz were measured by auto-balanced bridge method using an impedance analyzer (HP4294A). Ferroelectric hysteresis loops were investigated at room

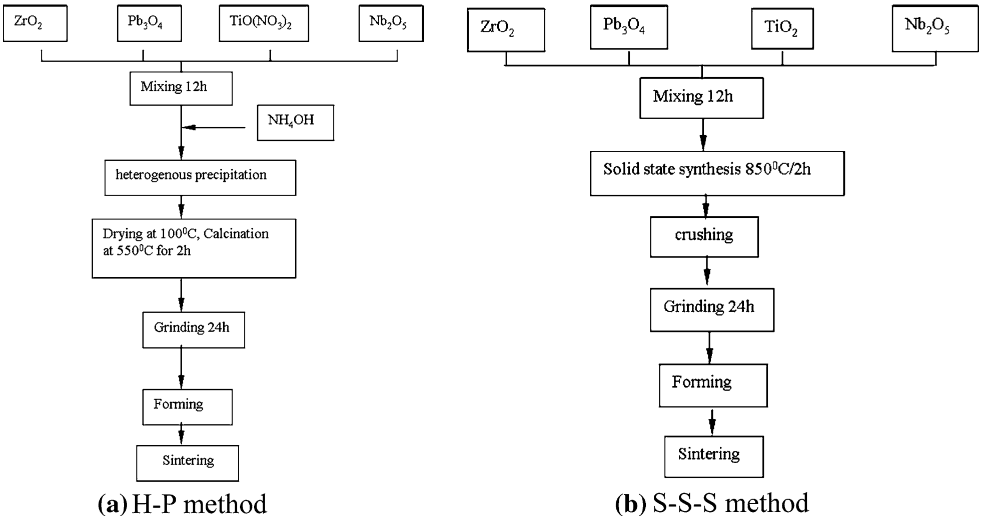


Fig. 1 Flow chart of H-P method (**a**) and S-S-S method (**b**)

temperature on a ferroelectric apparatus (TF Analyzer 2000, AIXACCT Company). Measurements of dielectric breakdown strength were carried out at room temperature for the samples in silicone oil using a plate tester and all samples have the same dimensions Φ14 mm × 1 mm. About 10 breakdown voltages were tested to compare the breakdown strength of two kinds of ceramic samples.

Results and discussion

Microstructure of the powders synthesized by H-P method

A TEM image of the powders prepared by S-S-S method is shown in Fig. 2(a). It is observed that the particles have a relative smooth and dense surface. A TEM image of the powders prepared by H-P method is shown in Fig. 2(b) and (c). It is obvious that there is a coating layer (about 10–20 nm thickness) on the surface of the particles after heterogenous precipitation process. In Fig. 3(a), the EDS spectra of the as-precipitated particles in Fig. 2(b) indicate that the intensity ratio of Ti peak to Zr peak at the edge field is much higher than that in the center field. This demonstrates that as-precipitated particles in Fig. 2(b) are a typical coated structure. The core particle is ZrO_2 particles and the coating layer is the $Ti(OH)_4$ precipitate. Similarly, In Fig. 3(b), the EDS spectra of the as-precipitated particles in Fig. 2(c) indicate that the intensity ratio of Ti peak to Pb peak at the edge field is much higher than that in the center field. This demonstrates that as-precipitated particles in Fig. 2(c) are a typical coated structure. The core particle is PbO particles and the coating layer is the $Ti(OH)_4$

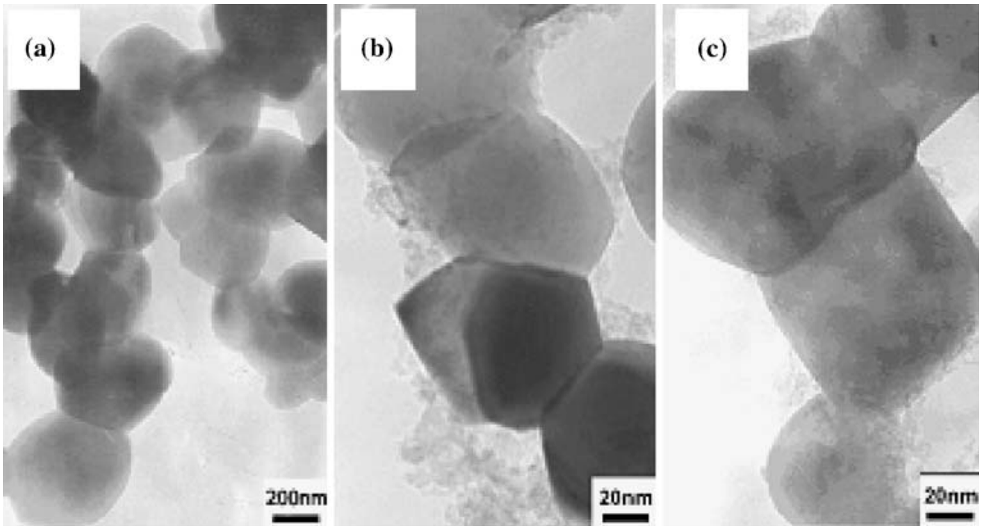


Fig. 2 TEM particles images of the S-S-S method (**a**) and the H-P method (**b** and **c**)

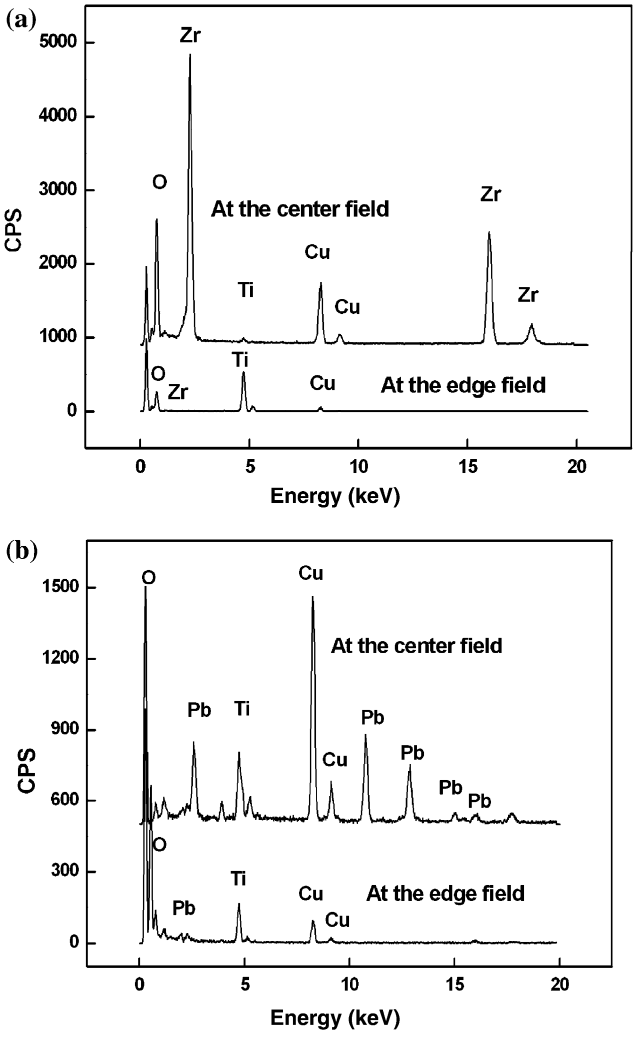


Fig. 3 EDS spectra of the coated particles

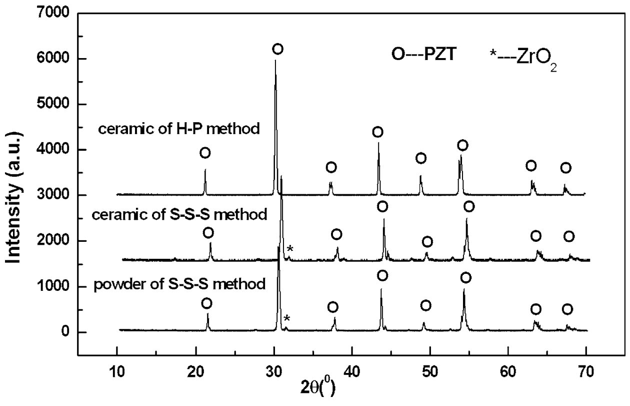


Fig. 4 XRD patterns of powders by S-S-S method and ceramics by H-P method & S-S-S method

precipitate It is obvious that $Ti(OH)_4$ precipitate grow on the surface of ZrO_2 and PbO particles to form a 10–20 nm coating layer. So we can assure that the Ti^{4+} was distributed homogeneously at the nanometric scale, which will bring an important effect on the properties and microstructure of the ceramics inevitably.

Phase characterization and microstructure of ceramics synthesized by H-P method

Figure 4 shows XRD patterns of powders synthesized by S-S-S method and ceramics synthesized by H-P method & S-S-S method. From the XRD pattern of powders synthesis by S-S-S method we can see that we acquired typical perovskite PZT phase by solid-state synthesis at 850 °C/2 h. In H-P method the goal of a heat treatment process at 550 °C/2 h was to decompose the $Ti(OH)_4$ precipitate into TiO_2. So after the heat treatment process at 550 °C/2 h, the XRD pattern of H-P powder was only the patterns of mixed oxide of ZrO_2, Pb_3O_4 and TiO_2. In fact, from Fig. 1 we can see that the synthesis and sintering process were happened simultaneously in H-P method's sintering process. So we give XRD pattern of ceramics by H-P method only.

In Fig. 4 it can be seen that Zr-rich PZT phase is obtained by both the H-P method and the S-S-S method. From Fig. 4 we can also see that there is a faint ZrO_2 diffraction peak in ceramics synthesized by S-S-S method, which denotes that a little second phase (ZrO_2) was separated out because of the volatilization of PbO in process of high temperature synthesis and high temperature sintering process in S-S-S method. The percentage of the perovskite phase is estimated using the following equation:

$$X_{\mathrm{perovskite}(\%)} = \left(\frac{I_{(110)\mathrm{perovskite}}}{I_{(110)\mathrm{perovskite}} + I_{(111)\mathrm{ZrO_2}}}\right) \times 100\% = \frac{1849}{1849 + 91} = 95.31\% \quad (4)$$

where $I_{(110)\mathrm{perovskite}}$ and $I_{(111)\mathrm{ZrO2}}$ are the intensity of the (110) peak of the perovskite phase and the intensity of (111) peak of the ZrO_2 phase, respectively. By comparing the XRD patterns, we can see that the ZrO_2 phase-free single phase Zr-rich PZT ceramics is synthesized by H-P method, which can prove that there is almost no PbO volatilization in process of H-P method. The reason of no PbO volatilization in process of H-P method was attributed to be origin from the synthesis and sintering process happened simultaneously in H-P method's sintering process, which decreased the chance of PbO volatilization in synthesis process**.** Since no PbO volatilization is assumed in the H-P method which experienced a calcination process at only 550 °C. We need not to consider any excess of

PbO in the H-P method. Figure 5 shows the microstructure of the ceramics synthesized by the two methods. We can see that the grain size of the H-P method is more homogeneous and fine than that by S-S-S method

Properties of Zr rich PZT ceramics synthesized by H-P method

Figure 6 shows the curve between density and sintering temperature of two kinds of ceramics. From Fig. 6, we see that we can obtain compact ceramics in a wide temperature range from 1280 °C to 1300 °C with the same sintering time 1.5 h. When temperature exceeded 1300 °C, the density decrease gradually because of the increasing PbO evaporation in the sintering process and the degree of PbO evaporation can be montored by testing the weight loss. We can also deduce that the density of ceramics synthesized by H-P method is higher than that by S-S-S method. Figure 7 shows the dielectric properties and the dissipation factor of the ceramics synthesis by two routes. We can see that the Curie temperature and the dissipation factor of the ceramics synthesized by H-P method are lower than that by S-S-S method.

Figure 8 shows the ferroelectric properties of the ceramics synthesized by two routes. We can see that the remnant polarization of the ceramics synthesized by H-P method is higher than that by S-S-S method. Also, the coercive field of the ceramics synthesized by H-P method is slightly higher than that by S-S-S method. The different electric properties of the ceramics synthesized by two methods are list in table 1. For convenience of comparing, the properties of another $Pb_{0.99}Nb_{0.02}(Zr_{0.965}Ti_{0.035})O_3$ ceramics were listed in Table 1 simultaneously, which was fabricated by hydroxide coprecipitation under hot-press and reported by Li Guo et al. [18]. The reason we use their data is because the composition they chose was the same as ours. We can see that the ceramics prepared by H-P method and hydroxide coprecipitation under hot-press method are possessed the same excellent properties, though the cost of ceramics

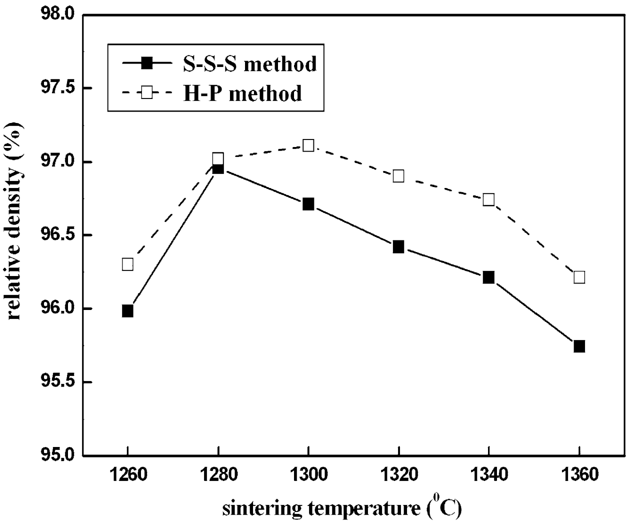


Fig. 6 Curve between density and sintering temperature of Zr rich PZT ceramics

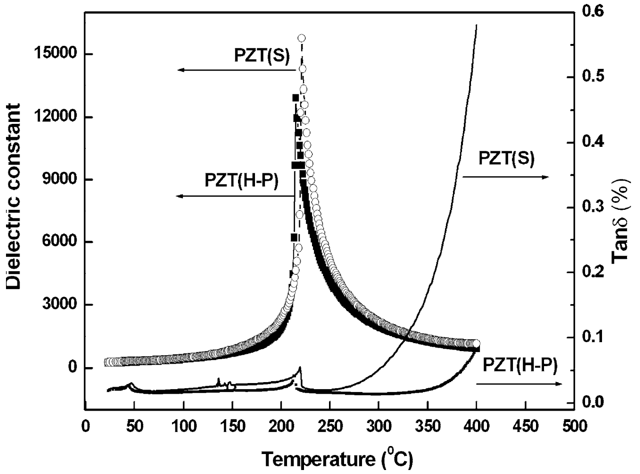
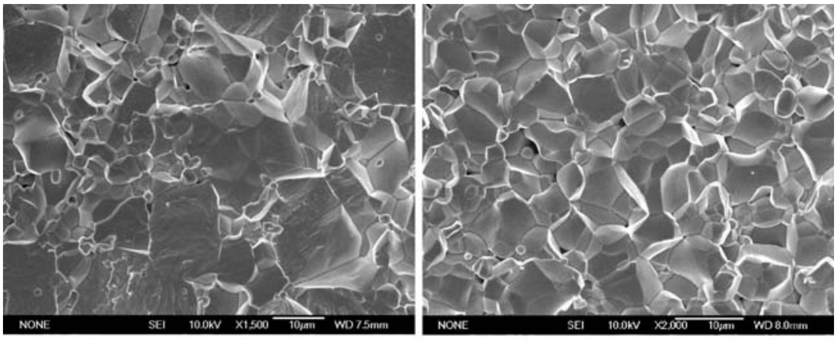


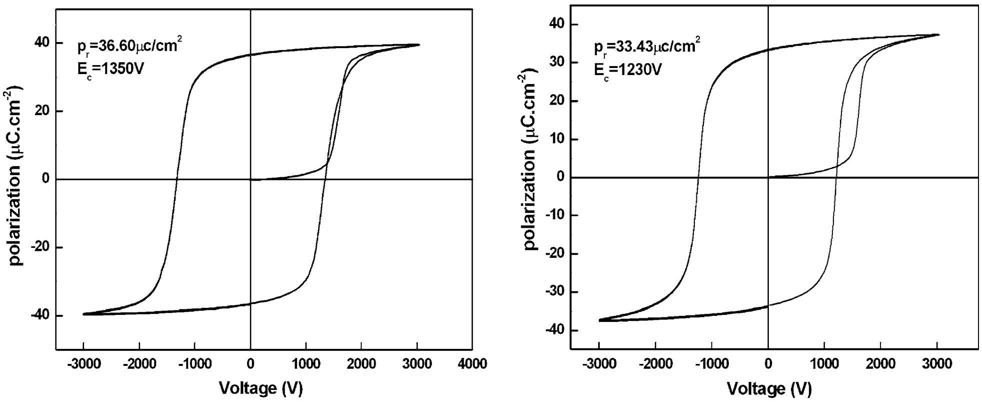
Fig. 7 Dielectric constant and Dissipation factor of ceramics synthesized by two routes



S-S-S method (sintered at 1300°C/1.5h) H-P method (sintered at 1300°C/1.5h)

Fig. 5 Microstructure of ceramics synthesized by two routes

Fig. 8 Hysteresis loops of Nb doped Zr-rich PZT ceramics by two routes



(A) S-S-S method **(B)** S-S-S method

Table 1 Properties of ceramics synthesized by two routes and reports

Samples	ε_{33}^{T}	Tanδ	Density(g/cm^3)	d_{33}(pc/N)	E_b (kV/mm)	E_c (V/mm)	P_r(μc/cm^2)
H-P (1300 °C/1.5 h)	305	0.022	7.6–7.7	65–70	6–7	1350	36.6
S-S-S (1280 °C/1.5 h)	297	0.019	7.7–7.8	62–64	4.5–5.5	1230	33.4
Hot-Press (1130 °C/2 h)[18]	350	0.02	7.7–7.9	60–70	16	1140	~30

prepared by hydroxide coprecipitation under hot-press method is much more expensive and output of ceramics prepared by hydroxide coprecipitation under hot-press method is much less. The evident difference of dielectric breakdown strength between ceramics prepared by hydroxide coprecipitation under hot-press method and H-P method may origin from the testing method and testing size of sample. In Table 1 we can deduce that the electric properties of the ceramics synthesized by H-P method are more excellent than that by S-S-S method. The dielectric breakdown (E_b) increased markedly from about 5 kV/mm to 6.5 kV/mm. This is crucial to electrical ceramics because the energy density per unit volume of capacitor, according to the equation: $w = 1/2\varepsilon_0\varepsilon_r E_b^2$, is dependent on the square of E_b. Therefore, the energy density per unit volume of capacitor made by ceramics synthesized by H-P method is $6.5^2/5^2 = 1.7$ times higher than that by S-S-S method. It is obvious that a substantial gain in charge storage can be realized if E_b of the dielectric has been improved.

Conclusion

The ZrO_2 phase-free single phase Zr rich $Pb_{0.99}Nb_{0.02}(Zr_{0.965}Ti_{0.035})O_3$ ceramics were successfully synthesized by H-P method. There is no faint ZrO_2 diffraction peak in ceramics synthesized by H-P method, which proves that there is almost no PbO volatilization in process of H-P method. The reason of no PbO volatilization in process of H-P method was attributed to be origin from the synthesis and sintering process happened simultaneously in H-P method's sintering process, which decreased the chance of PbO volatilization in synthesis process. The microstructure of the ceramics synthesized by H-P method was more homogeneous and fine than that by S-S-S method. The sintering density, the ferroelectric properties and the E_b of ceramics synthesized by H-P method are more outstanding than that by S-S-S method. From the process of H-P method, we can see it can ensure both the chemical homogeneity and the low cost in mass production, which combines the merits of traditional solid mixed reaction method and the liquid routes. The research work indicates that the heterogenous precipitation method is an excellent method to synthesize the Zr-rich PZT ceramics.

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