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Fabrication and electrical properties of low temperature sintering $Ba(W_{0.5}Cu_{0.5})O_3$ doped PSZT piezoelectric speaker

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To improve the sinterability and piezoelectric properties of $Pb_{0.98}Sr_{0.02}(Mg_{1/3}Nb_{2/3})_{0.275}(Ni_{1/3}Nb_{2/3})_{0.10}(Zr_{0.25}Ti_{0.375})O_3$ (PSZT) based ceramics, $Ba(W_{0.5}Cu_{0.5})O_3$ (BWC) doped solid phase synthesis was applied in this paper . The piezoelectric speakers with the BWC doped PSZT composition were fabricated and characterized. The low-temperature fabrication process, the microstructure, the phase structure and the electrical properties of the thus prepared ceramics were investigated. The results show that an addition of BWC considerably improves the sinterability of PSZT based ceramics, and, the sintering temperature consequently decreases from 1150 to 950 °C. This may be attributed to the promotion in the easiness of liquid-phase sintering. The 0.10 wt. % BWC doped ceramics sintered at 950 °C obtains the optimal piezoelectric properties with d_{33} of 564 pC/N, K_p of 0.66, Q_m of 46, tan δ of 0.0123, ε_p of 3109, respectively. Then, the piezoelectric speakers sintered at 950 °C show the favorable characteristics with a higher SPL of 80.33 dB and a lower THD of 32.42%. Those results show that the BWC doped PSZT ceramics is a promising material for practical application.

Key words : Sintering, Dielectric properties, Piezoelectric properties, Ferroelectric properties, Speaker.

Introduction

Lead-based perovskite solid solutions (PZT) have been widely used in various electronic devices, including piezoelectric actuators, sensors, transformer and acoustic transducers because of their good dielectric and piezoelectric properties [1, 2]. Speakers have many advantages, which are portable, good acoustic fidelity, low driving voltage and low noise etc. The ceramics suitable for the application of speakers should generate large displacement. It need the materials have high piezoelectric constant (d_{33}), high dielectric constant (ε_r), low dielectric loss (tanδ) and low mechanical quality factor (Q_m), etc [3].

Recently, PZT based ceramics have too high sintering temperature (1100 °C), which induces evaporation of PbO and serious pollution on the environment during the sintering process [4]. Therefore, low-temperature processing is one of the most important techniques for suppressing the compositional change, reducing the energy consumption and decreasing the environmental pollution during the multilayer piezoelectric fabrication process. As one of low-temperature sintering techniques, the addition of oxides and compounds such as glasses and metal oxides which have low melting point for liquid-phase sintering [5, 6]. However, some research results have indicated that piezoelectric properties are often deteriorated by low-temperature sintering with addition of sintering aid. Therefore, it is very important to select a suitable sintering aid and to disperse homogeneously a small amount of sintering aid in the matrix powders in order to improve the piezoelectric properties and reliability [7, 8]. However, a lot of work has been done to study the properties of the piezoelectric ceramics. There is a small amount of work that can investigate characteristics of the piezoelectric devices.

In this work, BWC was selected as a sintering aid and additives were applied for low-temperature fabrication of the PSZT based ceramics, and their microstructures, phase structure, ferroelectric and piezoelectric properties were investigated. On the other hand, the piezoelectric speakers with various structures were fabricated and the characteristics were measured. The aim of this work is to show that the multilayered piezoelectric speakers with favorable properties can be successfully fabricated.

Experimental Procedure

PSZT were synthesized from Pb_3O_4, $SrCO_3$, ZrO_2, TiO_2, Nb_2O_5, NiO, $MgCO_3$, Li_2CO_3, $BaCO_3$, WO_3, CuO using conventional ceramics process. All the original materials were analytically pure. To compensate the loss of lead during the sintering, excess Pb_3O_4 was added in the original materials. Dosing was adopted according to the stoichiometry of $Pb_{0.98}Sr_{0.02}(Mg_{1/3}Nb_{2/3})_{0.275}(Ni_{1/3}Nb_{2/3})_{0.10}(Zr_{0.25}Ti_{0.375})O_3$ + 0.8 wt.% Pb_3O_4 + 0.375 wt.%

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Li_2CO_3 + x wt.% $Ba(W_{0.5}Cu_{0.5})O_3$, where x = 0.00 wt.%, 0.05 wt.%, 0.10 wt.%, 0.15 wt.%, 0.20 wt.%, respectively. Appropriate amounts of those materials were milled in alcohol with zirconia balls for 12 h. As-prepared PSZT based powders mixtures were pressed under a pressure of 10 MPa to produce disc-shape pellets with 15 mm in diameter and about 1.5 mm in thick, with 5 wt.% polyvinyl alcohol (PVA) as a binder. After drying process, the mixtures were calcined at 800 ºC for 2 h to form pure perovskite structure powders. The pellets were sintered at a rate 3-5 ºC/min to temperatures in a range from 940 to 970 ºC for 4 h with Pb_3O_4 powder atmosphere. For the electrodes, the sintered samples were polished and silver paint was coated on both of the faces to serve as electrodes at 850 ºC.

Phase structure of the ceramics was measured by x-ray diffraction (XRD) (D/max-2200, Rigaku, Japan, Cu $K\alpha$) at room temperature. Surface microstructures of the ceramics were observed using a scanning electron microscopy (SEM) (model Quanta200, FEI Co). Density is measured by the Archimedes method with distilled water. The dielectric properties of the silver-coated samples were measured as a function of temperature at 0.1, 1 and 10 kHz by using an Agilent 4294A impedance analyzer connected to a computer automatic measurement. The heating rate was 2 ºC/min from room temperature to 300 ºC. The piezoelectric constant (d_{33}) was measured at room temperature using a quasi static piezoelectric d_{33} meter (ZJ-3d, China).

The piezoelectric ceramics bimorph were fabricated by using the tape-casting technique, and then were sintered at 950 ºC for 4 h in a sealed alumina crucible. The sintered samples were polished after an ultrasonic cleaning in an ethanol bath. Silver-paste was coated to piezoelectric ceramics speaker with dimensions with 15 mm in diameter and about 1.5 mm in thick on both sides by the screen printing method. Then piezoelectric ceramics speaker subsequently fired at 850 ºC for 30min. The piezoelectric ceramics bimorph were poled at 280 ºC for 5 min under a dc electric field of 1 kV/mm in air.

Results and Discussion

Fig. 1 shows the XRD pattern of PSZT ceramics sintered at 950 ºC as a function of BWC content. Apparently it can be seen from Fig. 1 that no second phase can be found. The rhombohedra phase is observed at room temperature when the BWC content is below 0.10 wt. %. The specimens with 0.10 wt. % BWC content showed the splitting of (002) and (200) peaks implying the tetragonal phase. It can be noted that the formation of BWC solid solution is beneficial for the diffusion of ions and lower the sintering temperature of the ceramics [9, 10].

The BWC content influences not only the phase

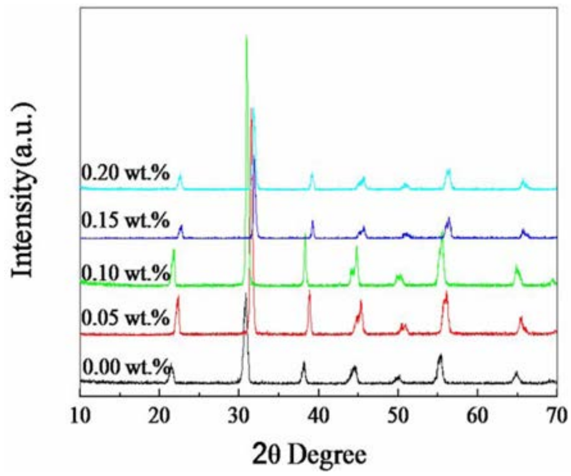

Fig. 1. XRD pattern of PSZT ceramics sintered at 950 ºC as a function of BWC content.

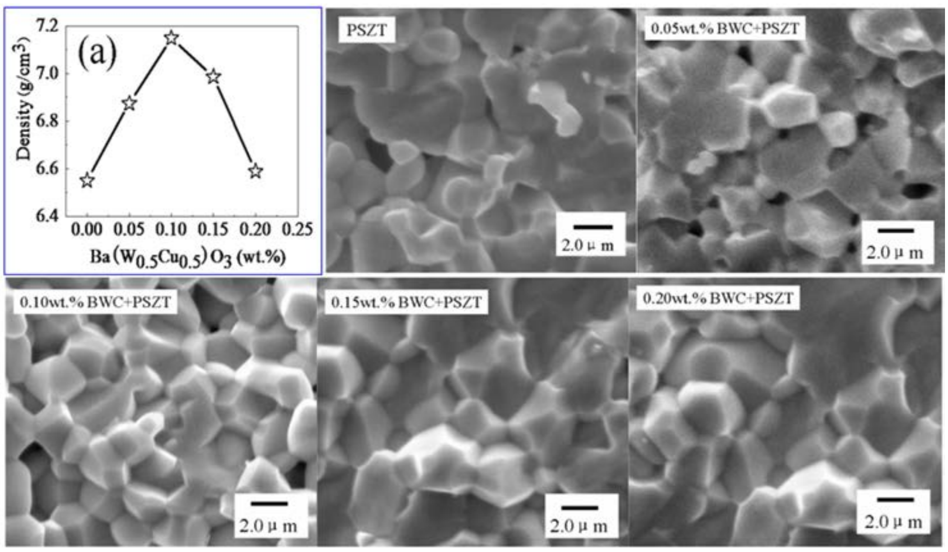

Fig. 2. The density and SEM images of PSZT ceramics sintered at 950 ºC as a function of BWC content.

composition of PSZT ceramics, but also the density and microstructure. Fig. 2(a) shows the density of PSZT ceramics sintered at 950 ºC as a function of BWC content. All samples were sintered at 950 ºC for 4 h. PSZT ceramics without BWC could not be fully dandified at sintering temperature lower than 950 ºC. The saturated densities of approximately 7.15 g/cm^3 were obtained by an addition of BWC sintering aid in the temperatures of 950 ºC. As BWC content increased, the density of the PSZT ceramics was not well developed, the density decreased and thus the porosity increased. Fig. 2 depicts the SEM photographs of PSZT ceramics and their densities of different amount of BWC. It showed that for the samples synthesized from 0.10 wt. % BWC content, the grain was well crystallized. The grain boundary was sharp and the grain size was uniform. These results indicated that 0.10 wt. % of BWC was optimal for preparation of well PSZT ceramics. Thus, the addition of BWC sintering aid markedly improved the sinterability of PSZT ceramics, resulting in reduction in sintering temperature by approximately 200 ºC. This is well consistent with the XRD result and the electrical properties discussed later.

Fig. 3 show the piezoelectric constant (d_{33}), the electromechanical coupling factor (k_p), and the mechanical quality factor (Q_m) values of PSZT ceramics sintered at 950 ºC as a function of BWC content, measured at room temperature. The d_{33} increases from 440 to 564 pC/N with increasing BWC content. The PSZT ceramic with 0.10 wt% BWC reaches maximum d_{33} values, which is induced by doping optimum BWC content. The k_p and Q_m change the opposite sense with different amounts of BWC. Firstly k_p increases when the content of BWC increases. The maximum value of 0.66 appears at x = 0.10 wt%. After that, k_p decreases with increasing BWC content. In contrast, Q_m first decreases with the maximum value of 89 obtained at the same value of x, then Q_m decreases with increasing BWC content. The minimum value of Q_m amounts to 46 at x = 0.10 wt. %.

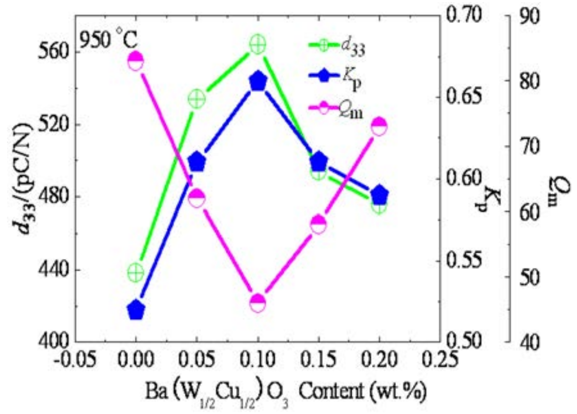

Fig. 3. The piezoelectric constant (d_{33}), the electromechanical coupling factor (k_p), and the mechanical quality factor (Q_m) values of PSZT ceramics sintered at 950 ºC as a function of BWC content.

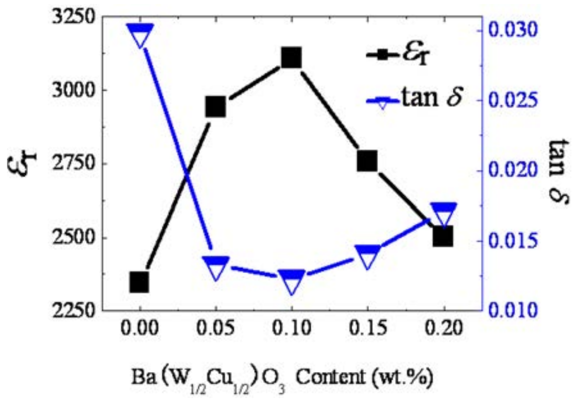

Fig. 4. The dielectric constant (ε_r) and dielectric loss (tan δ) values of PSZT ceramics as a function of BWC content.

Fig. 4 plots the dielectric constant (ε_r) and dielectric loss (tan δ) values of PSZT ceramics as a function of BWC content, measured at room temperature and 1 kHz. ε_r value increases with increasing the BWC content. Moreover, the tan δ value decreases with an increase in BWC content, which is due to the dense microstructure caused by the introduction of BWC.

Table 1. The electrical properties of Ba ($W_{1/2}Cu_{1/2}$)O_3-doped ceramics.

Sintering temperature (ºC)	Contant (wt.%)	d_{33} (pC/N)	K_p	Q_m	tanδ	ε_r	Sintering temperature (ºC)	Content (wt.%)	d_{33} (pC/N)	K_p	Q_m	tanδ	ε_r
	0.00	427	0.50	89	0.0356	2163		0.00	438	0.52	83	0.0299	2344
	0.05	498	0.58	69	0.0152	2678		0.05	534	0.61	62	0.0133	2940
940	0.10	540	0.61	58	0.0168	2930	950	0.10	564	0.66	46	0.0123	3109
	0.15	488	0.58	73	0.0229	2471		0.15	494	0.61	58	0.0141	2757
	0.20	473	0.57	79	0.0328	2205		0.20	476	0.59	73	0.0171	2501
	0.00	451	0.53	79	0.0242	2359		0.00	563	0.56	73	0.0213	2489
	0.05	482	0.57	83	0.0389	2191		0.05	468	0.54	91	0.0554	2077
960	0.10	513	0.60	76	0.0229	2596	970	0.10	502	0.56	89	0.0261	2296
	0.15	478	0.56	84	0.0336	2174		0.15	450	0.54	126	0.0450	1959
	0.20	458	0.55	97	0.0394	1951		0.20	445	0.52	142	0.0823	1911

The maximum value and minimum value of ε_r and tan δ are 3109 and 0.0123, respectively, as listed in Table 1. Enhanced electrical properties of PSZT ceramics should be attributed to the optimum BWC content and the dense microstructure, as shown in Fig. 2. The maximum density of specimens was shifted to lower temperature side according to the increase of the amount of BWC addition. During sintering, the presence of BWC liquid phase enhances the density, which leads to the decrease of the energy loss and improvement of the electrical properties. Because $BaCO_3$, WO_3 and CuO reacts and forms the liquid phase of BWC at about 870 °C, the density of specimens at low-temperature is enhanced by liquid phase produced [11].

In order to prevent the depolarization in the operating temperature range of the piezoelectric devices, the high Tc of 250 °C or higher is needed for piezoelectric materials. Fig. 5 shows the temperature dependence of the dielectric behavior of 0.10 wt% BWC doped PSZT ceramics sintered at 950 °C, measured at 1 kHz. It can be seen from Fig. 5 that the Curie temperature of 244 °C is obtained. This Curie temperature is high enough to contribute to the general stability of material characteristics for multilayer piezoelectric sound applications during operation process [12].

Fig. 6 shows the bipolar polarization hysteresis and strain electric field loops for 0.10 wt% BWC doped PSZT ceramics sintered at 950 °C. It can be observed in Fig. 6(a) that the 0.10 wt.% BWC doped PSZT ceramics exhibit the better ferroelectric properties with a remnant polarization of $P_r = 21.26$ μC/cm^2 and a coercive field of $E_c = 13.53$ kV/cm, indicating a higher degree of orientation of the ferroelectric domain near the 0.10 wt.% BWC doped PSZT composition. The variation of hysteresis strains with the amount of BCW is consistent to those of the P-E hysteresis loops. The *S-E* curves of the composition displays butterfly-shaped hysteresis curve for normal ferroelectrics in Fig. 6(b).

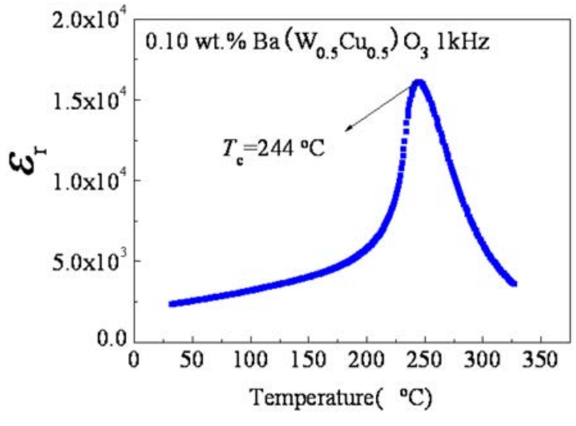

Fig. 5. The temperature dependence of the dielectric behavior of 0.10 wt % BWC doped PSZT ceramics sintered at 950 °C and measured at 1 kHz.

Fig. 7 shows the structure of the BWC doped PSZT based diaphragm. It consists of a BWC doped PSZT based ceramics layer (diameter d = 10 mm; ceramics thickness, 0.05 and 0.065 mm), Ag layer (diameter = 9.00 mm), and Metal layer (stainless steel diaphragm) plate (diameter D = 12.00 mm; thickness = 0.05 mm). The metal plate is attached to one side of the BWC doped PSZT based disk. Miniaturization of the BWC doped PSZT based diaphragms are very beneficial to improve the properties of piezoelectric ceramics speakers.

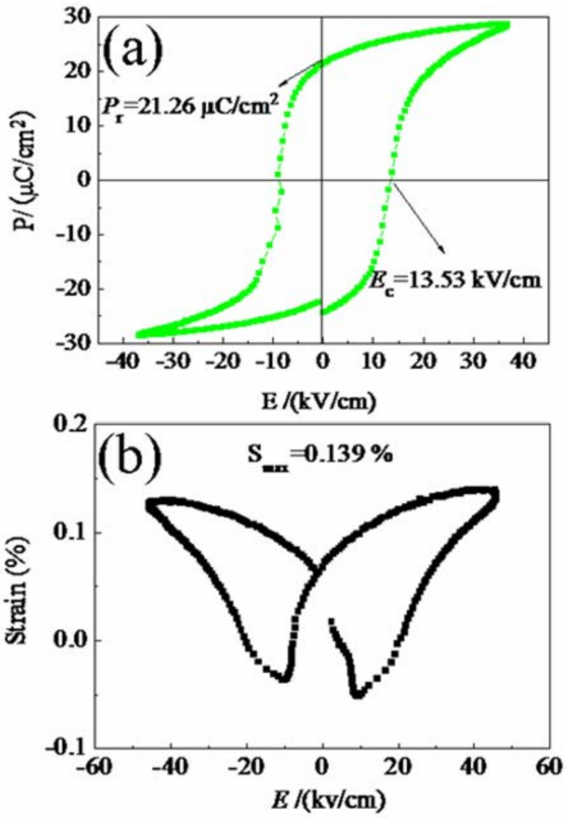

Fig. 6. The bipolar polarization hysteresis and strain electric field loops for 0.10 wt % BWC doped PSZT ceramics sintered at 950 °C.

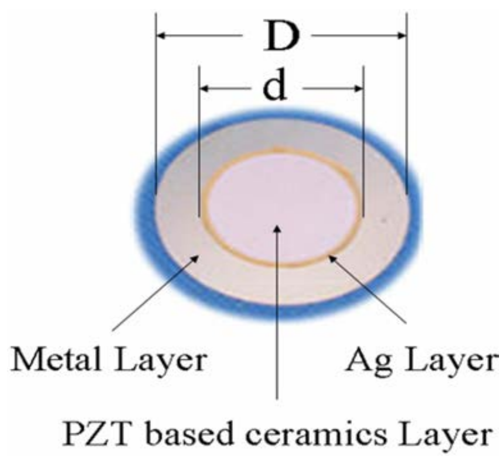

Fig. 7. The structure of the BWC doped PSZT based diaphragm.

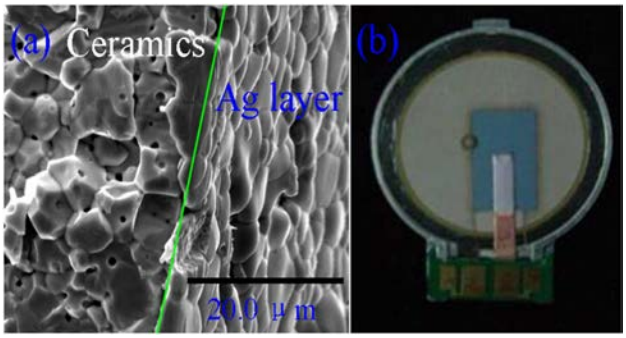

Fig. 8. The photographs of the 0.10 wt % BWC doped PSZT ceramics membranes and speakers.

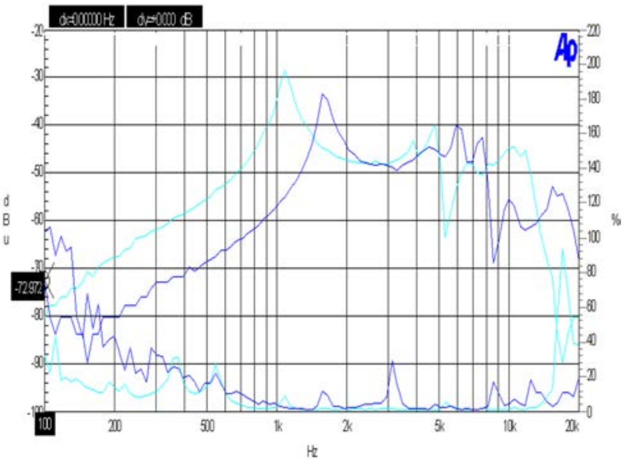

Fig. 9. The Sound Pressure Level (SPL) and Total Harmonic Distortion (THD) of the PSZT based speakers as a function of frequency in the range of 100-20000 Hz.

The 0.10 wt. % BWC doped PSZT ceramics sintered at 950 °C possess good electrical properties, which was selected as the materials for fabricating piezoelectric speakers. The piezoelectric speakers were prepared using the 0.10 wt. % BWC doped PSZT ceramics membranes with diameters of 10 mm and thicknesses of 0.050-0.065 mm obtained by using tape-casting technique. Fig. 8 shows the photographs of the 0.10 wt. % BWC doped PSZT ceramics membranes and speakers. The surface SEM photographs of the disk sintered at 950 °C show that the disks are fully densied with fairly uniform microstructures, clear grain boundary and no obvious pores. The uniform microstructure is helpful to enhance the mechanical strength of piezoelectric ceramics, which is very beneficial to the practical application, because piezoelectric ceramics usually require a high mechanical force and strain.

Fig. 9 shows the Sound Pressure Level (SPL) and Total Harmonic Distortion (THD) of the PSZT based speakers as a function of frequency in the range of 100-20000 Hz. It was found that lower value (72.972 dB) and higher THD (102.930%) of SPL for the speaker with 0.05 mm (in blue) is obtained at 1.75 kHz, which is slightly lower than that (SPL ≥ 80 dB) of the sound device applications. However, the SPL of the speaker with 0.065 mm thickness (in cyan) reaches a high SPL of 80.332 dB at 1.2 kHz and lower THD of 32.4219%, which is satisfied with the sound device applications. The results show that the 0.10 wt% BWC doped PSZT based ceramics speakers have good electro-acoustic properties which can basically satisfy the requirements of practical applications.

Conclusions

$Ba(W_{0.5}Cu_{0.5})O_3$ doped $Pb_{0.98}Sr_{0.02}(Mg_{1/3}Nb_{2/3})_{0.275}(Ni_{1/3}Nb_{2/3})_{0.10}(Zr_{0.25}Ti_{0.375})O_3$ based piezoelectric ceramics with dense microstructure and good electrical properties have been prepared by ordinary sintering process. The results showed that BWC sintering aid improved the sinterability signicantly, density and the properties of PSZT based ceramics and could decrease the sintering temperature from 1200 to 950 °C. The 0.10 wt. % $Ba(W_{0.5}Cu_{0.5})O_3$ doped PSZT based ceramics sintered at 950 °C exhibited the favorable electrical properties, which were listed as follows: d_{33} = 564 pC/N, k_p = 0.66, Q_m = 46, tan δ = 0.0123, ε_r = 3109, T_c = 244 °C, P_r = 21.26 μC/cm^2 and E_c=13.53 kV/cm. The piezo electric speakers with diameter d = 10 mm single layer and a thickness of 0.065 mm with 0.10 wt.% Ba $(W_{0.5}Cu_{0.5})O_3$ doped PSZT based ceramics were fabricated by the tape-casting. The piezoelectric speaker sintered at 950 °C exhibited higher SPL of 80.332 dB at 1.2 kHz and lower THD of 32.4219%, which is very suitable for the requirements of multilayer piezoelectric speaker practical applications.

Acknowledgments

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