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Aging behavior and electrical properties of low-temperature sintered (Ba, Ca)(Ti, Zr)O_3-Ba(Cu, W)O_3 ceramics and plate loudspeaker

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ABSTRACT

Lead-free $(1-x)$wt.% $(Ba_{0.85}Ca_{0.15})(Zr_{0.10}Ti_{0.90})O_3 - x$ wt.% $(Ba(Cu_{0.5}W_{0.5})O_3$ (BCZT − x wt.% BCW) piezoelectric ceramics were prepared by solid-state reaction. The phase structure of the ceramics showed that the orthorhombic–tetragonal phase boundary was identified in the range of $1.2 \le x \le 1.6$ wt.%. The dense microstructure and optimal electrical properties of the ceramics were obtained at $x = 1.2$ wt.%. Fatigue behavior of the ceramics was also investigated as a function of temperature and keeping time, where the BCZT − 1.2 wt.% BCW materials were found to possess improved fatigue characteristic. In addition, the sound pressure level (SPL) of 16.0 mm length × 16.0 mm width × 0.1 mm piezoelectric loudspeakers using lead-free BCZT ceramics with 1.2 wt.% BCW content at drive voltage of 10–20 V was more than 80 dB at frequency of 2.2–20.0 kHz. These results indicated that the 98.8 wt.% BCZT − 1.2 wt.% BCW ceramics was potential for piezoelectric loudspeaker applications.

1. Introduction

Barium titanate $BaTiO_3$ (BT) ceramics have attracted considerable attentions for the wide applications in capacitor, ferroelectric and piezoelectric devices [1–4]. Tremendous efforts for morphotropic phase boundary (MPB) have been made to promote the piezoelectric properties of $BaTiO_3$-based materials by different methods [5–9]. The newly discovered $Ba(Zr_{0.2}Ti_{0.8}) - x(Ba_{0.7}Ca_{0.3})TiO_3$ (BZT − xBCT) based ceramics have been actively investigated due to their excellent piezoelectric properties (with $d_{33} = 500$–620 pC/N) by forming a triple point of a paraelectric cubic phase, ferroelectric rhombohedral and tetragonal phases close to morphotropic phase boundary, which intrigues the research interest of most scientists for replacing lead-containing PZT materials [10,11].

Recently, much attention has been given to improving density and electrical properties of BZT − xBCT based ceramics [12,13]. The density has been effectively improved by different synthesis methods, such as solid state reaction [14–16], hydrothermal [17,18] and sol–gel methods [19,20]. In addition, the construction of R–T phase boundary by tuning component was carried out in order to high-performance BZT − xBCT based ceramics. Among those, adjusting both Ca and Zr were necessary to improve the piezoelectric properties of $BaTiO_3$ ceramics [21,22]. For example, Tian et al. reported that the substitution of Ca^{2+}/Zr^{4+} to replace Ba^{2+}/Ti^{4+} in $(Ba_{1-x}Ca_x)(Zr_yTi_{1-y})O_3$ (BC_xZ_yT) solid solutions can cause a light change in T_C, but has greatly deceased orthorhombic to tetragonal (T_{O-T}) transition temperature, which is of great value in improving the temperature stability of piezoelectric materials [23,5–7,11,16,21]. It is well known that doping oxides as a sintering aid are an effective way to decrease the sintering temperature and improve the dense microstructure of piezoelectric materials, such as, ZnO [24], CuO [25], MnO_2 and La_2O_3 [26] and so on. They were also introduced into BCZT based ceramics to obtain high-performance. Up to now, BZT − xBCT materials were found to possess the same limitation as that of BT materials, which was first discovered as a piezoelectric ceramics but was now mostly used as a dielectric material rather than a piezoelectric material mainly because of its low Curie temperature ($T_c \sim 93$ °C) and high sintering temperature (ST ∼ 1450 °C), which hindered the commercial processing and practical applications of BZT − xBCT based ceramics [2,3,10,14,23]. Considerable research has been investigated to decrease the sintering temperature, but at the cost of

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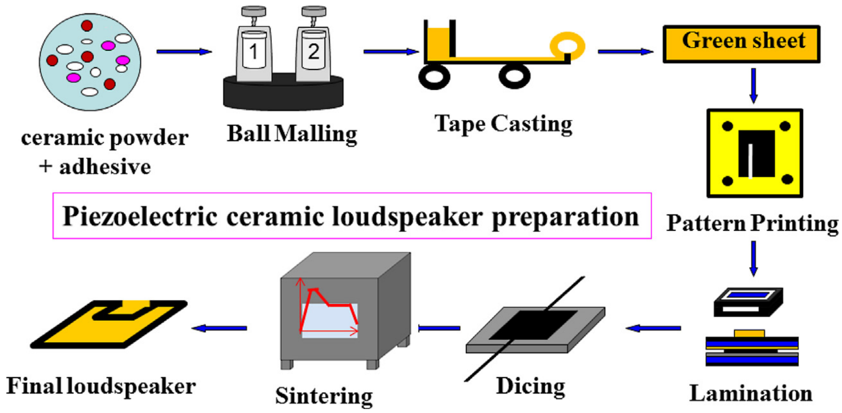

Fig. 1. Flow-process diagram of BCZT – 1.2 wt.% BCW ceramic loudspeakers.

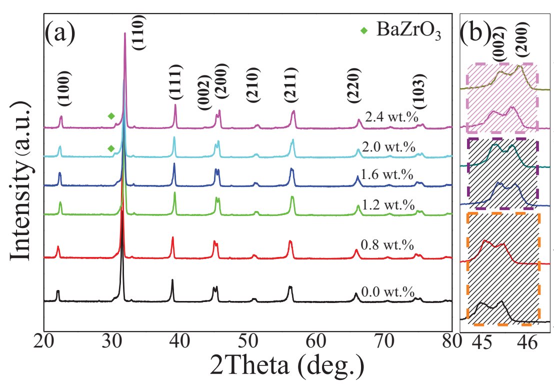

Fig. 2. XRD patterns of the BCZT – x wt.% BCW ceramics calcined at 1180 °C and sintered at 1220 °C.

reduced piezoelectric properties [24–26]. Adding sintering aids is a simple and effective method to lower the sintering temperature. $Ba(Cu_{0.5}W_{0.5})O_3$ (BCW) with perovskite structure as a sintering aid has been used to lower the sintering temperature of BCZT ceramics with improved properties, because it readily forms a liquid phase that assists densification and microstructure development due to its relatively low melting point [27,28]. In piezoelectric plate loudspeakers, high voltage difference caused by high vibration velocity can be obtained when a voltage is applied at both ends of the piezoelectric material with high d_{33}. So the voltage difference is converted into a bending force which is converted into high sound pressure level. However, few researcher reports fatiguing behavior of BCZT-BCW ceramics and BCZT-BCW based plate loudspeakers with favorable characteristic.

$Ba(Cu_{0.5}W_{0.5})O_3$ solid solution and $(Ba_{0.85}Ca_{0.15})(Ti_{0.9}Zr_{0.1})O_3$ (BCZT) – x wt.% BCW ceramics were prepared by solid-state reaction. Effect of BCW as the sintering aid on phase structure, electrical properties, temperature and time stability of BCZT – x wt.% BCW ceramics were systematically investigated, and the physical mechanisms for the enhanced electrical properties were also discussed. Moreover, lead-free piezoelectric loudspeakers were also fabricated using BCZT – 1.2 wt.% BCW material.

2. Experimental procedure

2.1. Sample preparation

$(1-x)$wt.% $(Ba_{0.85}Ca_{0.15})(Zr_{0.10}Ti_{0.90})O_3-x$ wt.% $Ba(Cu_{0.5}W_{0.5})O_3$ ceramics (x = 0.0, 0.8, 1.2, 1.6, 2.0 and 2.4 wt.%) were synthesized using conventional mixed oxide approach. $BaCO_3$ (≥99%, Sinopharm Chemical Reagent Co., Ltd.), $CaCO_3$ (≥99%, Sinopharm Chemical Reagent Co., Ltd.), ZrO_2 (≥99%, Sinopharm Chemical Reagent Co., Ltd.), TiO_2 (≥98%, Sinopharm Chemical Reagent Co., Ltd.), CuO (≥99.5%, Sinopharm Chemical Reagent Co., Ltd.), and WO_3(≥99%, Sinopharm Chemical Reagent Co., Ltd.) powders were used as starting materials. $Ba(Cu_{0.5}W_{0.5})O_3$ was first prepared at 730 °C for 3 h and form a sintering aid with low melting point, which is benefit to shrinking weighing error and reducing production time for BCZT-BCW based plate loudspeakers [27]. The powders were weighed according to the stoichiometric composition and mixed for 24 h using ball milling in alcohol solution with Yttrium stabilized Zirconia media. The amount of impurity has been considered when calculating and weighing the powders stoichiometrically. The mixed powders were dried and calcined at 1180 °C for 6 h. These powders were milled again, dried, and granulated by adding 5 wt.% polyvinyl alcohol (PVA) solution and uniaxially pressed into pellets with a diameter of 1.5 cm under 100 MPa. Following binder burnout at 500 °C, the samples were sintered at 1220 °C for 4 h in air. For electrical measurements, the samples were polished and then electrode on the parallel surfaces using fire-on silver paste (No. PC-8070, Kunming Xizhi Electrical Materials Co., Ltd.) at 850 °C for 30 min. Poling was carried out at 2 kV/mm for 10 min at 50 °C in silicon oil. The poling electric field was kept on until the temperature decreased to room temperature. All experiments are performed after 24 h at ambient temperature.

2.2. Fabrication of piezoelectric loudspeakers

Manufactural procedure of piezoelectric loudspeaker is shown in Fig. 1. The square structure with dimensions L16 × W16 × T0.1 mm is selected and fabricated plate piezoelectric loudspeaker. 98.8 wt.% $(Ba_{0.85}Ca_{0.15})(Zr_{0.10}Ti_{0.90})O_3$ – 1.2 wt.% $Ba(Cu_{0.5}W_{0.5})O_3$ materials (2.0 kg) was prepared by the conventional mixed-oxide method. The mixtures were milled in ethanol using Yttrium stabilized Zirconia ball as media in a polyethylene jar for 24 h. The mixed slurry was dried at 80 °C and calcined at 1180 °C for 6 h. The calcined powders were then grounded again under the same condition to obtain fine powders with uniform size [29]. After drying, green sheets consisted of calcined powder and organic binder (No. FN-18, Fuzhou Bond Co., Ltd.) were prepared by a conventional tape-casting technique (No. BHLY-GD-C-8m, Guangdong Fenghua Aavanced Technology (Holding) Co., Ltd.). After binder burn-out at 550 °C, the samples were sintered at 1220 °C for 4 h in air. The external electrodes were coated on both sides of the loudspeakers and fired at 850 °C for 30 min. The optimal poling voltage (1.8–2.5 kV/mm) was obtained by a large amount of experiments for 30 min at 50 °C in silicon oil. All experiments are performed after 24 h at at ambient temperature.