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Structure and electrical properties of Li-doped $BaTiO_3$–$CaTiO_3$–$BaZrO_3$ lead-free ceramics prepared by citrate method

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ABSTRACT

1 wt% Li-doped $0.75BaTiO_3$–$0.15CaTiO_3$–$0.1BaZrO_3$ (BCZT) ceramics were prepared by the citrate method. XRD measurement showed that pure perovskite BCZT precursor powders are obtained calcined at 600–700 °C, which exhibit rather homogeneous microstructure morphology with nm-scale grain size. The sintered BCZT ceramics exhibit pure perovskite structure with composition locating at rhombohedral side around the morphotropic phase boundary (MPB). Oxide doping and citrate method exert great influences on microstructure and electrical properties of the Li-doped BCZT ceramics. All the synthesized ceramics exhibit excellent dielectric and ferroelectric properties. The Li-doped BCZT ceramics calcined at 700 °C and sintered at 1500 °C exhibit the best dielectric, ferroelectric and piezoelectric properties. The high piezoelectric response of the synthesized Li-doped BCZT ceramics is considered as relating to the MPB effect, Li-doping and wet chemical synthesis method.

1. Introduction

Lead-based ferroelectric perovskites, represented by $(1-x)PbZrO_3$–$xPbTiO_3$ (PZT), have dominated the field of industrial piezoelectric applications, including sonars, buzzers, motors and ultrasonic cleaners, owing to their superior piezoelectric, dielectric, and electromechanical properties especially with the compositions around the morphotropic phase boundary (MPB) [1,2]. The MPB of PZT is known to locate at the composition of $x = 0.48$, which is considered as a region connecting different ferroelectric phases, allowing facile domain orientation reversal during the poling process. Further modifications using acceptor and donor dopants provide us the wide range of piezoelectric compositions we have today [3]. However, such lead-based materials contain almost 60 wt% lead, which tends to release into the environment. This occurs during calcination and sintering processes, and after usage accompanied recycling and waste disposal, causing the environmental pollution and harming to human health. Hence, the high toxicity of PZT and the growing demand of replacing these lead containing piezoceramics have driven considerable research of environment-friendly materials [4].

Over the past years, much efforts have been done to search for lead-free piezoceramics to substitute PZT. Recent reports on lead-free piezoelectrics are focus on three perovskite families: $K_{0.5}Na_{0.5}NbO_3$ (KNN) [4,5], $Na_{0.5}Bi_{0.5}TiO_3$ (NBT) [6,7], and $BaTiO_3$ (BT) [8,9]. In the KNN and NBT systems, the alkali components become highly unstable and easily to evaporate during high temperature sintering, which makes it difficult to maintain chemical stoichiometry and leads to the deterioration of electrical properties [5]. As a classical perovskite ferroelectric, BT is another lead-free ceramic system and possesses good composition controllability. It is well known that BT is widely used as a commercial dielectric material rather than piezoelectric material due to its high dielectric property and low piezoelectric coefficient ($d_{33} = 191$ pC/N) [10]. Recently, Liu and Ren [11] reported a Ca and Zr co-doped BT system with extraordinarily high d_{33} ($\sim$620 pC/N), which can be comparable with PZT-5H. The high piezoactivity stems from the tricritical triple point-like MPB composition [11]. Since then, further studies have focused on doping [12,13], sintering temperature [14], piezoelectric [15], pyroelectric [16], optical [17] properties, and manufacturing process [18,19].

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However, most Ba(Zr$_x$Ti$_{1-x}$)O$_3$–(Ba$_y$Ca$_{1-y}$)TiO$_3$ (BZT–BCT) piezoelectric ceramics reported as yet are mainly fabricated by the conventional solid-state reaction method [11–17], which requires rather high calcination temperature (~1300 °C). The solid state sintering usually produces inhomogeneous microstructure and impurity phases, which may deteriorate electrical properties. By contrast, wet chemical synthesis method is beneficial to obtain high chemical purity, rather dense microstructure, and better homogeneity [18]. As a common chemical solution synthesis method, citrate method is essentially a polymeric precursor method, which uses citrate acid and water as complex agent and solvent, respectively, leading to improved homogeneity and stabilized compositions [20].

So far as we know, there are few reports on the microstructure and piezoelectric properties of the BZT–BCT ceramics derived from the citrate method. In this work, the composition 0.75BaTiO$_3$–0.15CaTiO$_3$–0.1BaZrO$_3$ (BCZT) was fabricated by the citrate method, and LiNO$_3$ was doped to adjust piezoelectric properties of the BCZT ceramics. Such composition locates around the reported tricritical triple point MPB composition and exhibits excellent electrical properties [21]. The influences of ceramics processing and chemical doping on crystal structure and electrical properties of the BCZT ceramics were studied and their possible causations were interpreted.

2. Experimental procedure

The 1 wt% LiNO$_3$-doped 0.75BaTiO$_3$–0.15CaTiO$_3$–0.1BaZrO$_3$ (BCZT) ceramics were prepared by the citrate method. Ba(NO$_3$)$_2$ (99.5%), Ca(NO$_3$)$_2$·4H$_2$O (99%), Zr(NO$_3$)$_4$·5H$_2$O (99.5%), C$_{16}$H$_{36}$O$_4$·Ti (98%) and LiNO$_3$ (99.9%) were used as starting materials. In this method, the mole ratio of the citric acid to the total metal cations was 1:1. The weighed amount of citric acid was dissolved into deionized water and the pH value was adjusted to 7–9 by ammonia water. The designed amount of tetrabutyl titanate was slowly added into the citric acid solution and stirred at 70 °C to form a transparent aqueous solution. Various nitrates were then added according to the stoichiometric ratio and stirred at 80 °C to form a semitransparent precursor solution. The precursor solution was heated and dried to form a gel. The gel was pre-calcined at 300 °C for 2 h to eliminate the water, ammonia, citric acid and organics, eventually obtaining dark-brown powder. The powder was then calcined at 600–700 °C for 2 h to form perovskite BCZT. The calcined powders were cold dry-pressed uniaxially into pellet with 13 mm in diameter and 1.5 mm in thickness with the addition of appropriate amount of 8 wt% polyvinyl alcohol (PVA) solution as binder and then sintered at 1490 °C and 1500 °C for 2 h in a covered zirconium dioxide crucibles.

The sintered ceramics were polished to obtain flat and parallel surfaces. Crystal structure of the calcined Li-doped BCZT powders and sintered Li-doped BCZT ceramics was investigated by a Rigaku D/max-2500/PC X-ray Diffraction meter (XRD, Rigaku Corp., Japan) using the well-polished ceramics. Simultaneous thermogravimetric analysis (TG) and differential scanning calorimetry (DSC) analysis of the pre-calcined powder were carried out by a simultaneous thermal analyzer (TG–DSC, Setaram Instrumentation Corp., France), which was heated from room temperature to 1400 °C in air at a rate of 10 °C/min. Microstructure morphology of the calcined powders were observed by a Zeiss SupraTM 55 Sapphire Field Emission Scanning Electron Microscope (FESEM, Carl Zeiss Group, Germany). The medium diameter of the calcined powders was measured by a BT-9300S laser scattering particle analyzer (Dandong Bettersize Instruments Ltd., China). For electrical properties characterization, silver paste was coated on both surfaces of the well-polished ceramics and fired at 550 °C for 30 min to provide robust electrodes. Dielectric property was measured by a computer-controlled TH2818 Automatic Component Analyzer under a weak oscillation level of 1 V_{rms} (Changzhou Tonghui Electronic Co. Ltd., China). For piezoelectric property measurement, the ceramics were poled at room temperature under different electric field between 0.5 and 3 kV/mm with an interval of 0.5 kV/mm for 5 min in silicon oil to investigate the influences of polarization electric field on piezoelectric properties. Piezoelectric properties were measured by a ZJ-6A Berlincourt-type quasi-static d_{33}/d_{31} meter (Institute of Acoustics, Chinese Academy of Sciences, Beijing, China) and a TH2826 Wide Frequency LCR Meter (Changzhou Tonghui Electronic Co. Ltd., China) using the resonance-antiresonance method. Detailed electrical properties measurement procedures were described elsewhere [22].

3. Results and discussion

3.1. Citrate method processing

Fig. 1 shows the simultaneous TG–DSC curves and the first order partial differential of the TG curve of the Li-doped BCZT pre-calcined powder. The TG–DSC curves could be helpful to determine the temperature of the solid state reaction. The strongest endothermic peak appears at 469.6 °C, accompanied by serious weight loss and extremum of derivative thermogravimetry, indicating the decomposition of nitrates. Due to the dynamic measurement characteristic of DSC and the expense time for the decomposition of nitrates, two small endothermic peaks appear subsequently at 528.9 and 599.5 °C, which also may be correlated with the combustion of residual organics. In addition, a minor exothermic peak appears at 612.6 °C, which can be attributed to the solid state reaction and the initial crystallization [23]. The weight loss reaches nearly 40% when the temperature increases to 700 °C, indicating that most organic components and nitrates have decomposed. A wide weak exothermic peak appears around 880 °C may be also correlated with the solid state reaction since such reaction usually is a slow weak exothermic process depending on diffusion and chemical reaction. Based on the TG–DSC analysis, the calcining temperature is chosen between 600 and 700 °C considering the dynamic nature of thermal analysis.

Fig. 2 shows XRD patterns of the Li-doped BCZT powders calcined between 600 and 700 °C. All the calcined powders exhibit typical perovskite structure, and almost no impurity phase can be detected. Pure perovskite structure Li-doped BCZT has already formed at calcining temperature of 600 °C, where the nitrates and organics have decomposed and the solid state reaction begins as shown by the TG–DSC analysis. No apparent difference in the phase formation is observed of the powders calcined between 625 °C and 700 °C. It is clearly evident that perovskite structure can be formed well below calcining temperature of 700 °C by the citrate method, which is much lower than that used by the conventional solid state reaction method (~1300 °C) [11,14]. The decreased calcining temperature obtained in this study can be attributed to the oxide doping, and small particle size, homogenous distribution and high activity of the precursor powders prepared by the citrate synthesis process.

Medium diameter and grain size of the calcined Li-doped BCZT powders are shown in Table 1, based on laser particle size analysis and XRD measurement of the (100), (110) and (111) diffraction reflections. The grain size was estimated by the Scherrer formula: $d = k\lambda/\beta\cos\theta$, where d is the grain size; k is the shape factor, 0.89; λ is the X-ray wavelength, 0.15406 nm; β is the full-width at half-maximum (FWHM) of the diffraction peak; θ is the Bragg's angle. Due to the detection limitation of the laser scattering particle analyzer, the medium diameter D_{50} of the particles is around μm-scale, which is different from the nm-scale values of grain size calculated by the Scherrer formula. Particle size tends to increase with the increase of calcining temperature; however, no simple regularity appears in this study. In order to detect exact particle size of the calcined Li-doped BCZT powders, FESEM

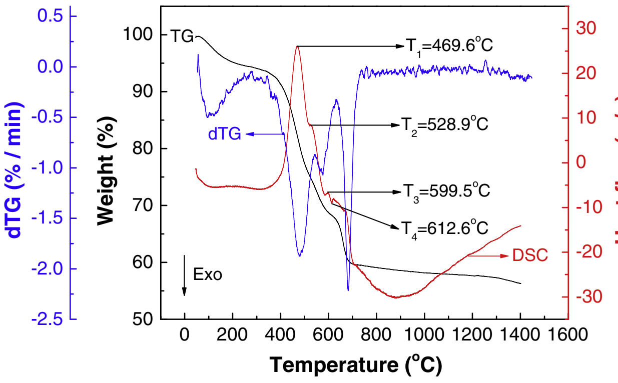

Fig. 1. Simultaneous TG–DSC curves of the Li-doped BCZT pre-calcined powder.