Journal of Alloys and Compounds 509 (2011) L359–L361

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: www.elsevier.com/locate/jallcom

Letter

Effect of dwell time during sintering on piezoelectric properties of $(Ba_{0.85}Ca_{0.15})(Ti_{0.90}Zr_{0.10})O_3$ lead-free ceramics

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ARTICLE INFO

Article history:
Received 12 July 2011
Received in revised form 4 August 2011
Accepted 5 August 2011
Available online 16 August 2011

Keywords:
Lead-free piezoelectric ceramic
Piezoelectric properties
Dwell time

ABSTRACT

In this letter, the effect of dwell time (1–6 h) during sintering on the piezoelectric properties is investigated for the $(Ba_{0.85}Ca_{0.15})(Ti_{0.90}Zr_{0.10})O_3$ ceramics. All ceramics sintered at different dwell time are of a pure phase, and its structure distortion is induced by too long dwell time. Their dielectric constant and remanent polarization increases and the coercive field decreases with increasing dwell time. An enhanced piezoelectric behavior ($d_{33} \sim 492$ pC/N and $k_p \sim 51.5\%$) is demonstrated for the BCTZ ceramic with an optimum dwell time of 5 h, owing to the structure distortion together with a dense microstructure and a larger grain size.

1. Introduction

Lead-free piezoelectric ceramics have been given to considerable attention as compared with $Pb(Zr,Ti)O_3$ (PZT) ceramics with the recent growing demand of global environmental protection [1–4]. Among these lead-free piezoelectric ceramics, most researchers pay much attention to (K, Na)NbO_3 (KNN) and $(Bi_{0.5}Na_{0.5})TiO_3$ (BNT) materials [1–6]. For example, a high d_{33} value of ~416 pC/N has been demonstrated in textured Li, Ta, Sb-modified KNN ceramics [1], and good piezoelectric properties have been induced by forming a solid solution between BNT and $BaTiO_3$ [6]. However, these lead-free ceramics prepared by normal sintering have a lower d_{33} value than those of Pb(Zr, Ti)O_3 ceramics [1–6], and especially KNN-based ceramics have a low density owing to the loss of K and Na during sintering and BNT-based ceramics exhibit a low depolarization temperature. Recently, $BaTiO_3$-based ceramics have attracted much attention in the field of piezoelectric ceramics due to its high d_{33} value [7–12], where the $BaTiO_3$ is often considered as a dielectric material owing to a low d_{33} value [13]. In 2009, a surprisingly d_{33} ($d_{33} \sim 620$ pC/N) value of ions-modified $BaTiO_3$ ceramics has been reported by Liu and Ren [7], confirming that $BaTiO_3$-based ceramics possess a high possibility of replacing these lead-based materials.

In the past, some methods have been used to improve the piezoelectric properties of $BaTiO_3$-based ceramics, for example, by the construction of phase boundary [7,11,12,14,15], the employment of site engineering [7,11,12], the use of different preparation techniques [14], and the sintering condition [15]. For the morphotropic phase boundary composition of 50[Ba(Zr,Ti)O_3–50(Ba,Ca)TiO_3)], its d_{33} is found to be a very high value of 580–600 pC/N [12]. Surprisingly high d_{33} values of ~350–460 pC/N have been reported for the $BaTiO_3$ ceramics prepared by different sintering techniques [16,17]. In the past, different sintering conditions strongly affect the electrical properties of piezoelectric ceramics [18–21]. Nevertheless the relationship between microstructure and electrical properties is still lacking for Ca and Zr-modified $BaTiO_3$ ceramics, where its microstructure is modified by changing the sintering condition (i.e., dwell time during sintering) in this work.

In this paper, the effect of dwell time during sintering on the piezoelectric properties of $(Ba_{0.85}Ca_{0.15})(Ti_{0.90}Zr_{0.10})O_3$ ceramics is studied. Enhanced piezoelectric properties of $d_{33} \sim 492$ pC/N and $k_p \sim 51.5\%$ are demonstrated for the $(Ba_{0.85}Ca_{0.15})(Ti_{0.90}Zr_{0.10})O_3$ ceramics by optimizing the dwell time during sintering, and the underlying physical mechanisms are also illuminated.

2. Experimental procedure

$(Ba_{0.85}Ca_{0.15})(Ti_{0.90}Zr_{0.10})O_3$ ceramics were prepared by the conventional solid-state reaction technique. Raw materials of $BaCO_3$ (99.0%), $CaCO_3$ (99.0%), ZrO_2 (99.0%) and TiO_2 (99.5%) were mixed with the addition of the ethanol for 24 h, dried and calcined at 1200 °C for 3 h, and then the powders were milled again for 24 h. After drying, the powders were pressed into 10 mm in diameter pellets and sintered at 1500 °C for the different dwell time of 1–6 h in air. All ceramics were poled at a room temperature of 40 °C in a silicon oil bath under a dc field of 4.0 kV/mm for 20 min. The phase structure in these ceramics was analyzed by using X-ray diffraction (DX-2000, China). The piezoelectric constant d_{33} of these ceramics was measured using a piezo-d_{33} meter (ZJ-3A, China). An impedance analyzer (Solartron Gain Phase Analyzer) was employed to characterize their dielectric properties. The dielectric behavior as a

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doi:10.1016/j.jallcom.2011.08.024

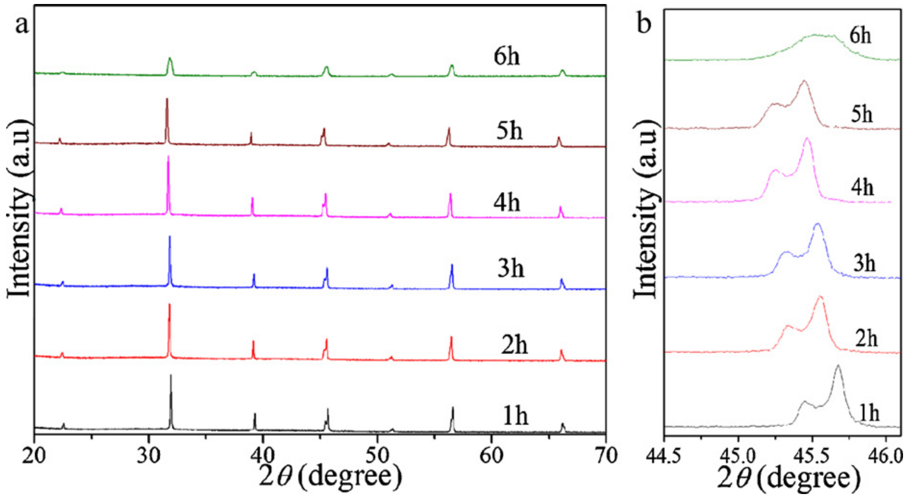

Fig. 1. (a) XRD patterns and (b) expanded XRD patterns in the 2θ range of 44.5–46.2 of BCTZ ceramics with different dwell time during sintering.

function of temperature was obtained using an *LCR* meter (HP 4980, Agilent, U.S.A.). Ferroelectric properties of these ceramics were studied by using the Radiant precise workstation (Radiant Technologies, Medina, NY).

3. Results and discussion

Fig. 1(a) plots the XRD patterns of BCTZ ceramics sintering at different dwell time. All ceramics are of a pure phase, and no secondary phases are detected in the range detected. However, the peak intensity of the BCTZ ceramic sintered at a dwell time of 6 h is weaker than those of these ceramics sintered at other dwell time. Fig. 1(b) shows the expanded XRD patterns of BCTZ ceramics sintered at different dwell time. The peak position of BCTZ ceramics is shifted to a lower angle with increasing the dwell time of 1–4 h due to the lattice distortion, and then is shifted to a higher angle with further increasing the dwell time of 5–6 h. Moreover, different peak shapes are also demonstrated for the BCTZ ceramic sintered at a dwell time of 6 h. The sintering condition (too long dwell time) affects the crystal structure of BCTZ ceramics in this work. Similar phenomenon has been observed for the lead-based ceramics [18].

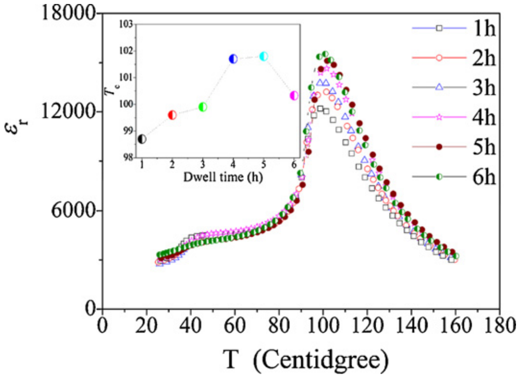

Fig. 2. Temperature dependence of the dielectric constant of BCTZ ceramics with different dwell time during sintering, where the insert is the T_c value as a function of dwell time.

Fig. 2 plots the temperature dependence of the ε_r in BCTZ ceramics with different dwell time, measured at the frequency of 10 kHz. There are two peaks for the BCTZ ceramics sintered at the dwell time of 1–5 h in the measurement temperature range of 25–160 °C, and two peaks are assigned to the coexistence of tetragonal and rhombohedral phases and the tetragonal to cubic phase transition (T_C), respectively. However, the coexistence of tetragonal and rhombohedral phases almost disappears for the ceramic sintered at a dwell time of 6 h, confirming the involvement of the structure distortion. The T_C value increases with increasing the dwell time when the dwell time is less than 6 h, and then slightly decreases with further increasing the dwell time (6 h), as shown in the insert of Fig. 2.

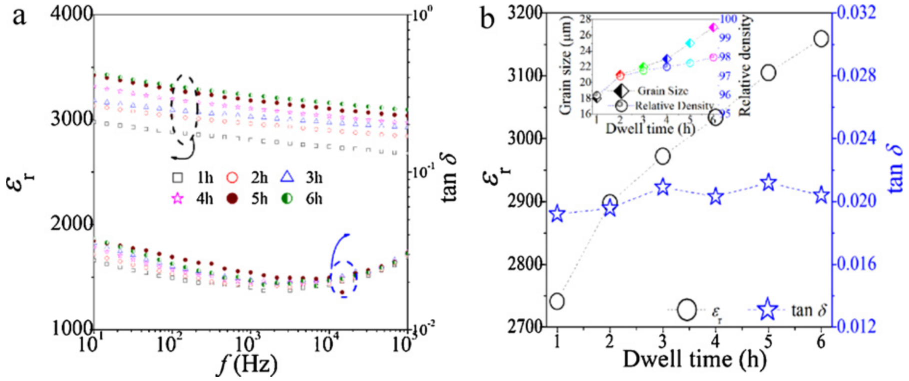

Fig. 3. (a) Dielectric properties of BCTZ ceramics with different dwell time during sintering as a function of measurement frequencies, and (b) ε_r and tan δ values of BCTZ ceramics as a function of dwell time, where the insert is average grain size and the relative density of BCTZ ceramics as a function of dwell time.

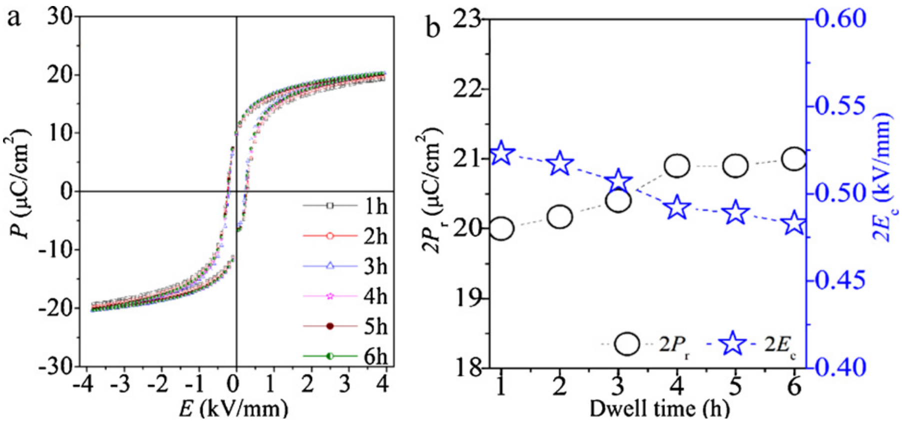

Fig. 4. (a) P–E loops and (b) $2P_r$ and $2E_c$ values of BCTZ ceramics with different dwell time during sintering.

Fig. 3(a) shows the dielectric properties of BCTZ ceramics with different dwell time during sintering as a function of measurement frequencies, measured at room temperature. The ε_r value increases with increasing the dwell time, while the dielectric loss ($\tan\delta$) slightly changes. Fig. 3(b) shows the ε_r and $\tan\delta$ values for the BCTZ ceramics as a function of dwell time, measured at 10 kHz. The ε_r value increases from ~2741 to ~3159 with increasing the dwell time of 1–6 h, and the $\tan\delta$ value is in the range of 1.92–2.12%. The insert of Fig. 3(b) shows the average grain size and the relative density of BCTZ ceramics as a function of dwell time. The average grain size and the density of these ceramics increase with increasing the dwell time due to the grain growth controlled by the boundary diffusion, confirming that the different dwell time can enhance the diffusion mechanism and promote the densification of these ceramics. This result is in agreement with reported results [18–21]. Therefore, the increase in ε_r value can be attributed to the larger grain size of BCTZ ceramics.

Fig. 4(a) plots the P–E loops of BCTZ ceramics as a function of dwell time, measured at room temperature and the frequency of 10 Hz. Saturated P–E hysteresis loops are demonstrated for all BCTZ ceramics in the present work. Fig. 4(b) plots the $2P_r$ and $2E_c$ values of BCTZ ceramics as a function of dwell time. The $2P_r$ value slightly increases with increasing the dwell time, while the $2E_c$ value decreases [18].

Fig. 5 shows the piezoelectric coefficient (d_{33}) and planar mode electromechanical coupling coefficient (k_p) of BCTZ ceramics as a function of dwell time. d_{33} And k_p values of BCTZ ceramics reach their maximum values of 492 pC/N and 51.5%, respectively. The largest d_{33} value of BCZT ceramics sintered at the dwell time of 5 h can be attributed to a structure distortion together with a dense microstructure and a larger grain size, where the structure distortion leads in the easier rotation of domain becomes when poled.

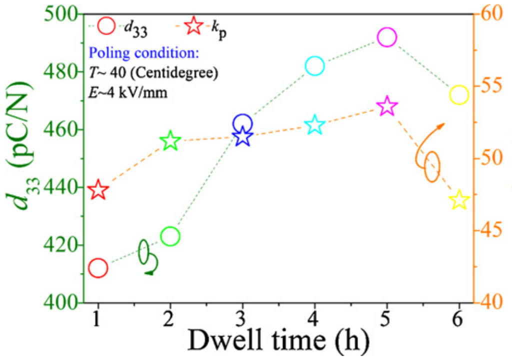

Fig. 5. Piezoelectric properties of BCTZ ceramics as a function of dwell time.

4. Conclusions

$(Ba_{0.85}Ca_{0.15})(Ti_{0.90}Zr_{0.10})O_3$ (BCTZ) lead-free ceramics with different dwell time have been prepared by the normal sintering. The dwell time affects the dielectric, ferroelectric, and piezoelectric properties of BCTZ ceramics. The T_c, ε_r, and P_r values of BCTZ ceramics increase, and the E_c value decreases with increasing the dwell time. The BCTZ ceramic with a optimum dwell time of 5 h has an improved piezoelectric behavior ($d_{33} \sim 492$ pC/N and $k_p \sim 51.5\%$), owing to a structure distortion together with a dense microstructure and a larger grain size.

Acknowledgements

Dr. Jiagang Wu gratefully acknowledges the supports of the introduction of talent start funds of Sichuan University (2082204144033), the National Science Foundation of China (NSFC Nos. 51102173, 50772068 and 50972001), the Foundation of Doctor Training Program in University and College in China (Nos. 20030610035, and 20080610020), and the National University of Singapore.

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