

## **Effects of CuO, Cr<sub>2</sub>O<sub>3</sub> and Fe<sub>2</sub>O<sub>3</sub> Doping on Phase Formation, Microstructure and Electric Properties of (Ba<sub>0.85</sub>Ca<sub>0.15</sub>)(Ti<sub>0.90</sub>Zr<sub>0.10</sub>)O<sub>3</sub> Ceramics**

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### **ABSTRACT**

The effects of CuO, Cr<sub>2</sub>O<sub>3</sub> and Fe<sub>2</sub>O<sub>3</sub> doping on the phase formation, microstructure and electric properties of (Ba<sub>0.85</sub>Ca<sub>0.15</sub>)(Ti<sub>0.90</sub>Zr<sub>0.10</sub>)O<sub>3</sub> (BCTZ) ceramics prepared by the combustion method were studied. Glycine was used as fuel and the ratio of raw material to fuel was 1:1.11. All samples were calcined and sintered at the temperatures of 1050°C and 1450°C for 2 h, respectively. The XRD data showed a pure perovskite structure with the coexistence of orthorhombic and tetragonal phases in all samples. The grain morphology of the ceramics exhibited irregular polyhedron shape and the average grain size was in the range of 15.5±0.9 to 42.8±2.2 μm. Samples of the BCTZ ceramics modified with Cu exhibited the highest density (5.79 g/cm<sup>3</sup>), the highest maximum dielectric constant (ε<sub>c</sub>=12500) and good ferroelectric properties (P<sub>r</sub>=12.6 μC/cm<sup>2</sup> and E<sub>c</sub>=2.5 kV/cm).

*Keywords: phase formation, microstructure, dielectric properties, ferroelectric properties*

### **INTRODUCTION**

(Ba<sub>0.85</sub>Ca<sub>0.15</sub>)(Ti<sub>0.90</sub>Zr<sub>0.10</sub>)O<sub>3</sub> (BCTZ) solid solution is one of the lead-free piezoelectric materials with a perovskite structure, which has received considerable attention. This is mainly due to their high piezoelectric coefficient (d<sub>33</sub>≥442 pC/N) around a morphotropic phase boundary (MPB). Moreover, BCTZ ceramics show good dielectric properties (ε<sub>r</sub>>2800 and ε<sub>m</sub>>10000) and remnant polarization (P<sub>r</sub>~9.43 μC/cm<sup>2</sup>) with the use of high calcination (1300-1350 °C) and sintering temperatures (1500-1550 °C) as well as very long dwell times (Wu *et al*, 2012; Liu *et al*, 2009) In recent years, methods that can reduce the firing temperature and improve the electrical properties have been studied by using doping material, including metal oxides such as CuO (Sun *et al*, 2015),

$\text{Fe}_2\text{O}_3$  (ZuO *et al.*, 2008), ZnO (Zhao *et al.*, 2015), MgO (Miao *et al.*, 2015) and  $\text{Cr}_2\text{O}_3$  (Wei *et al.*, 2015). It is well known that doping with these metal oxides helps to produce the liquid phase during the sintering process, which promotes densification and better grain morphology. T. Bongkarn and coworkers (Bongkarn *et al.*, 2016) prepared  $(\text{K}_{0.44}\text{Na}_{0.52}\text{Li}_{0.04})(\text{Nb}_{0.84}\text{Ta}_{0.10}\text{Sb}_{0.06})\text{O}_3$  (KNLNTS) ceramic with added  $\text{Fe}_2\text{O}_3$  (0-1.0 wt%) by the solid state reaction method. The results concluded that  $\text{Fe}_2\text{O}_3$  doped at 0.6 wt% increased the electrical properties ( $\epsilon_r \sim 2800$  and  $\epsilon_c \sim 7500$ ) and ferroelectric properties ( $P_r \sim 27.9 \mu\text{C}/\text{cm}^2$  and  $E_c \sim 9.9 \text{ kV}/\text{cm}$ ), which were higher than undoped KNLNTS ceramic. J. Wei and coworkers (Wei *et al.*, 2015) found that doping  $\text{Cr}_2\text{O}_3$  into  $\text{Bi}_{0.8}\text{Ba}_{0.2}\text{FeO}_3$  (BBFC) ceramic obtained good ferroelectric properties of  $P_r \sim 0.95 \mu\text{C}/\text{cm}^2$  which were higher than undoped BBFC ceramic. F. Azough and coworkers (Azough *et al.*, 2011) investigated CuO doped  $\text{Na}_{0.475}\text{K}_{0.475}\text{Li}_{0.05}\text{NbO}_3$  (NKLN) ceramics produced by the mixed oxide route. The results showed that the CuO doping decreased the sintering temperature of NKLN and increased the density to within 96% of the theoretical value. With CuO doping of 0.4 wt%, the ceramic exhibited a saturation polarization ( $P_s$ ) of  $30 \mu\text{C}/\text{cm}^2$ , remanent polarization ( $P_r$ ) of  $27 \mu\text{C}/\text{cm}^2$  and coercive field ( $E_c$ ) of  $1.0 \text{ kV}/\text{mm}$ .

In this research, we studied the phase formation, morphology and electrical properties of BCTZ ceramics modified by doping with 0.4 wt% of CuO,  $\text{Cr}_2\text{O}_3$  and  $\text{Fe}_2\text{O}_3$ , synthesized by the solid state combustion technique.

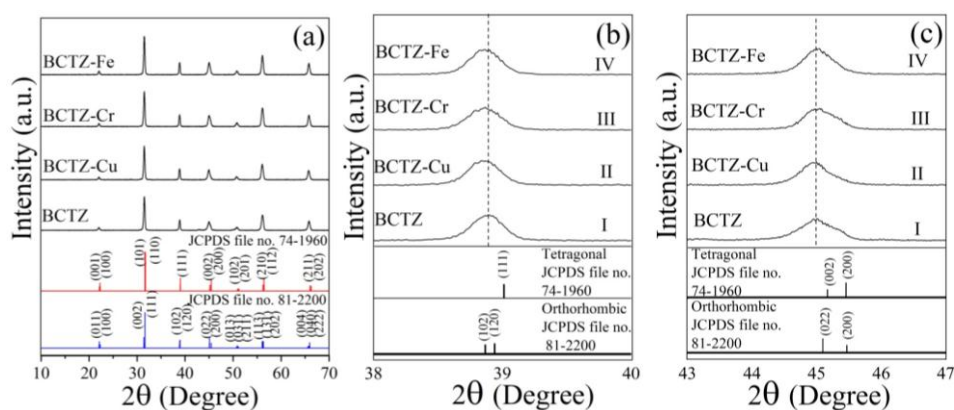
## EXPERIMENTAL

$(\text{Ba}_{0.85}\text{Ca}_{0.15})(\text{Ti}_{0.90}\text{Zr}_{0.10})\text{O}_3$  (BCTZ) doped with 0.4 wt% of  $\text{Fe}_2\text{O}_3$  (BCTZ-Fe), CuO (BCTZ-Cu) and  $\text{Cr}_2\text{O}_3$  (BCTZ-Cr) ceramics were prepared by the solid-state combustion method with glycine used as the fuel. High purity  $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ ,  $\text{BaCO}_3$ ,  $\text{TiO}_2$ , and  $\text{ZrO}_2$  were used as raw materials. The raw materials were weighed according to the desired stoichiometry and mixed by ball milling using ethanol as medium for 24 h. After that, the slurry was dried at  $90^\circ\text{C}$  and mixed with glycine at a ratio of 1:1.11 in an agate mortar. Next, the mixed powders were calcined at a temperature of  $1050^\circ\text{C}$  for 2 h (Kornphom *et al.*, 2016). The calcined BCTZ powders were mixed with  $\text{Fe}_2\text{O}_3$ , CuO and  $\text{Cr}_2\text{O}_3$  powders at ratios of 0.4 wt% in all samples. These compound powders were ball milled with a polyvinyl alcohol (PVA) for 12 h. Next, the powders were dried and pressed into pellets with a diameter of  $\sim 15 \text{ mm}$  and a thickness of  $\sim 1.2\text{-}1.4 \text{ mm}$  at  $80 \text{ MPa}$ . Pellets were sintered at  $1450^\circ\text{C}$  for 2 h in a sealed alumina crucible (Kornphom *et al.*, 2016). Subsequently, for electrical measurements, the

sintered samples were polished and painted with silver paste on both sides and fired at 500 °C for 15 min.

The phase structures of the sintered ceramics were analyzed using X-ray diffraction (XRD). The microstructures of the ceramics were studied using a scanning electron microscope (SEM). The density of the all sintered ceramics was measured by the Archimedes method. The dielectric constant and dielectric loss of the ceramics were measured by an LCR meter at a frequency of 1 kHz over a temperature range from 25 °C to 200 °C. The ferroelectric polarization hysteresis loops (P-E) were measured using a computer controlled modified Sawyer-Tower circuit.

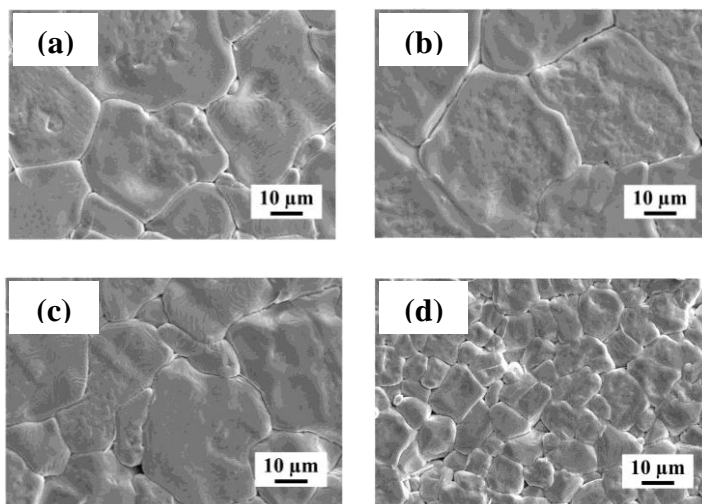
## RESULTS AND DISCUSSION



**Figure 1** XRD spectra of BCTZ, BCTZ-Cu, BCTZ-Fe and BCTZ-Cr ceramics in the  $2\theta$  range of; (a) 10-70°, (b) 38-40° and (c) 43-47°

Figure 1 (a) illustrates the XRD spectra of the BCTZ, BCTZ-Cu, BCTZ-Fe and BCTZ-Cr ceramics sintered at 1450 ° for 2 h, measured at room temperature in the  $2\theta$  range of 10-70°. A pure perovskite phase was formed for all samples, and no impurity phase can be found in the XRD peak. Figure 1 (b) and (c) shows the expanded XRD spectra of all samples at the  $2\theta$  angle of 38-40° and 43-47°. Generally, the characteristics of the orthorhombic phase (O) in the X-ray diffraction spectral (in accordance with JCPDS no. 81-2200) demonstrates dual peaks of (102)/(120)<sub>O</sub> and (022)/(200)<sub>O</sub> at a  $2\theta$  range of 39° and 45° while the tetragonal phase (T) (in accordance with JCPDS no. 74-1960) exhibits a single peak of (111)<sub>T</sub> at  $2\theta$  around 39° and dual peaks of (002)/(200)<sub>T</sub> around

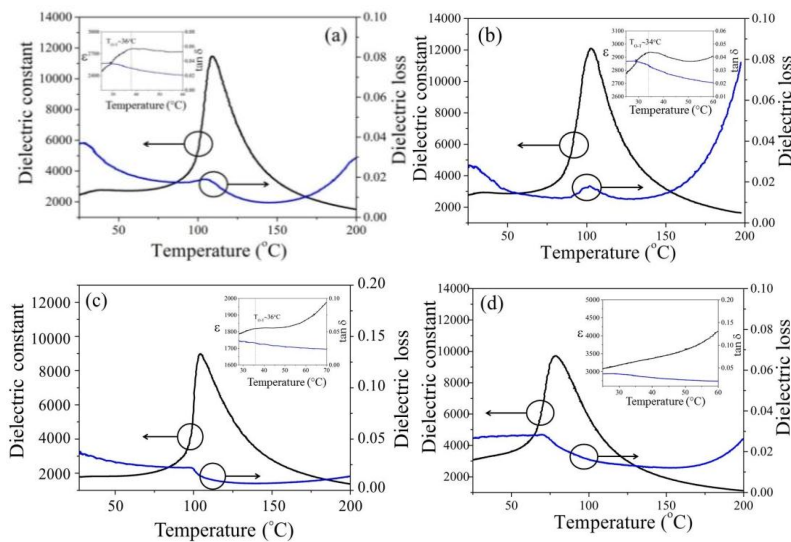
45°. In this study, the XRD peak of the BCTZ ceramics presented no symmetry peak at  $2\theta$  around 39° (Figure 1 (b) I) and dual peaks were not observed at  $2\theta$  around 45° (Figure 1 (c) I). These results suggest that the orthorhombic and tetragonal phases coexist in this composition. For BCTZ-Cu, BCTZ-Cr and BCTZ-Fe ceramics, the diffraction peaks of these ceramics showed a more non-symmetry peak (skewed to left side) and a slight move to a lower angle (Figure 1 (b) II-IV). Broader dual peaks were also observed at  $2\theta$  around 45° (Figure 1 (c) II-IV). These results suggest that these compositions still had coexisting phases (O+T) and the unit cell expanded.



**Figure 2** SEM micrographs of polished and thermal etched surface of sintered (a) BCTZ, (b) BCTZ-Cu, (c) BCTZ-Cr and (d) BCTZ-Fe

SEM micrographs of the samples are shown in Figure 2 (a)-(d). The grains of all ceramics exhibited irregular polyhedron shapes, and the grain growth tended to be anisotropic. The BCTZ ceramics showed large grains with a uniform distribution and were closely packed (Figure 2 (a)). Similar to BCTZ, BCTZ-Cu ceramic also showed a uniform grain distribution with larger grain sizes (Figure 2 (b)). In the case of the BCTZ-Cr ceramic, it exhibited larger grain sizes compared to BCTZ ceramics, a non-uniform grain distribution and pores on the surface (Figure 2 (c)). The increased grain size of BCTZ-Cu and BCTZ-Cr ceramics may be caused by the presence of oxygen vacancy that helps mass transport during the sintering process, which is similar to previous results (Chen

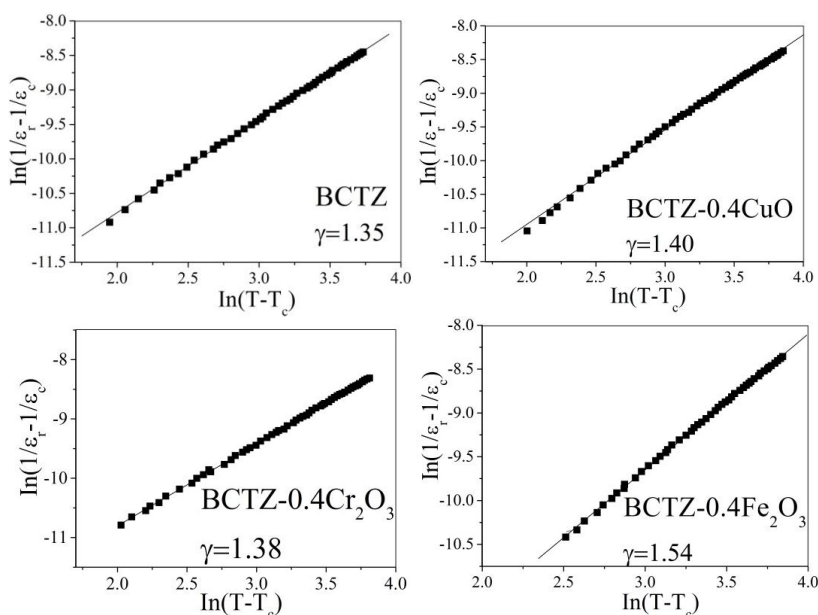
*et al.*, 2015). Compared with BCTZ ceramics, the BCTZ-Fe ceramic shows smaller grain size and small pores at the grain boundaries. This result suggested that  $\text{Fe}_2\text{O}_3$  may accumulate at the grain boundaries and suppressed the grain growth of the BCTZ ceramic (Figure 2 (d)) (Ma *et al.*, 2013). The average grain sizes were  $37.8 \pm 5.5$ ,  $42.8 \pm 2.2$ ,  $36.9 \pm 3.9$  and  $15.5 \pm 0.9$   $\mu\text{m}$  for BCTZ, BCTZ-Cu, BCTZ-Cr and BCTZ-Fe ceramics, respectively. The measured density of all samples was obtained by the Archimedes method. The values of the density and relative density of the samples are listed in Table 1. The highest density and relative density of  $5.79 \text{ g/cm}^3$  and 98.3% were obtained by the BCTZ-Cu ceramic. The measured density results corresponded well with the SEM results.



**Figure 3** Temperature dependence of dielectric constant and dielectric loss for the samples measured at 1 kHz; (a) BCTZ, (b) BCTZ-Cu, (c) BCTZ-Cr and (d) BCTZ-Fe

The temperature dependence of the dielectric behavior at 1 kHz of BCTZ, BCTZ-Cu, BCTZ-Cr and BCTZ-Fe ceramics sintered at  $1450$   $^{\circ}\text{C}$  for 2 h is displayed in Figure 3. The BCTZ ceramic showed two dielectric anomalies. The first peak appeared at a lower loss temperature of  $36$   $^{\circ}\text{C}$ , which corresponded to a phase transition from the orthorhombic ferroelectric phase to the tetragonal ferroelectric phase ( $T_{\text{O-T}}$ ). The second peak was observed at a higher temperature  $\sim 109$   $^{\circ}\text{C}$  which was related to the phase transition from tetragonal ferroelectric phase to cubic paraelectric phase ( $T_{\text{c}}$ ). Similar to BCTZ, the BCTZ-Cu and BCTZ-Cr ceramics showed two phase transitions as a function of temperature.

The  $T_{O-T}$  and  $T_c$  values of BCTZ-Cu and BCTZ-Cr ceramics are shown in Table 1. In contrast to BCTZ, BCTZ-Cu, and BCTZ-Cr, the BCTZ-Fe ceramics exhibited only one dielectric peak at  $T_c$  ( $\sim 78$  °C). The absence of a  $T_{O-T}$  transition may be attributed to the lattice distortion in the crystal structure. The  $T_{O-T}$  of all samples with different dopants are presented in the inset of Figure 3 (a)-(d). The  $\epsilon_r$  of all samples were in the range of 1790-3097, as shown in Table 1. The BCTZ-Cu ceramic showed the highest dielectric constant ( $\epsilon_c=12500$ ) and the low dielectric loss ( $\tan \delta$  at  $T_c = 0.017$ ). The values of the dielectric loss at room temperature ( $T_r$ ) and  $T_c$  are shown in Table 1. The dielectric properties corresponded to the morphology and density results.

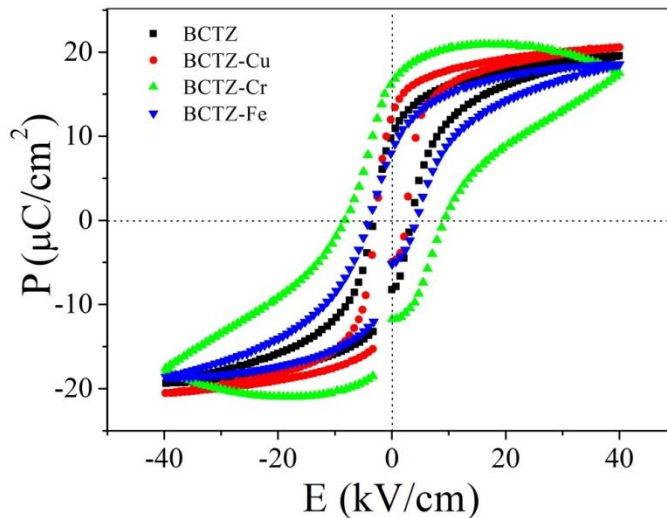


**Figure 4** The plots of  $\ln(1/\epsilon - 1/\epsilon_c)$  against  $\ln(T - T_c)$  at 1 kHz for the BCTZ, BCTZ-Cu, BCTZ-Cr and BCTZ-Fe ceramics

In addition, BCTZ ceramics exhibited a sharp dielectric curve at  $T_c$  (Figure 3 (a)). While for the BCTZ-Cu, BCTZ-Cr and BCTZ-Fe ceramics, the dielectric curve at  $T_c$  become broader when compared with undoped ceramics (Figure 3 (b)-(d)). This indicated that a diffuse phase transition was formed. A modified Curie-Weiss law (Uchino *et al.*, 1982; Ding *et al.*, 2009) can be used to described the diffuseness of the phase transition at  $T_c$ , as described by

$$\frac{1}{\varepsilon} - \frac{1}{\varepsilon_c} = (T - T_c)^\gamma / C$$

Where  $\varepsilon_c$  is the maximum value of the dielectric constant at  $T_c$ ,  $C$  is the Curie-Weiss constant and  $\gamma$  is the diffusion factor ( $1 < \gamma < 2$ , 1 and 2 are corresponding to normal ferroelectric and relaxor ferroelectric, respectively) (Ciomaga *et al.*, 2007). Plots of  $\ln(1/\varepsilon - 1/\varepsilon_c)$  as a function of  $\ln(T - T_c)$  are shown in Figure 4 (a)-(d) and the values of  $\gamma$  for all samples were obtained. In all calculations, the  $\gamma$  values of BCTZ-Cu, BCTZ-Cr, and BCTZ-Fe ceramics were higher than the BCTZ ceramic (Figure 4 (a)-(d)). This indicated that these samples exhibited an increasing in relaxor ferroelectric behavior. The increasing of the relaxor ferroelectric state in BCTZ-Cu, BCTZ-Cr, and BCTZ-Fe ceramics could be caused by a distortion of the crystal lattice owing to the generation of oxygen vacancies (Miao *et al.*, 2015).



**Figure 5** Polarization hysteresis loops of the BCTZ, BCTZ-Cu, BCTZ-Cr and BCTZ-Fe ceramics at room temperature under the electric field of 40 kV/cm

Polarization hysteresis loops of the BCTZ, BCTZ-Cu, BCTZ-Cr and BCTZ-Fe ceramics were measured at room temperature, as shown in Figure 5. The P-E loop of the BCTZ ceramic showed a slim and saturated curve. The remanent polarization ( $P_r$ ) and coercive field ( $E_c$ ) of the BCTZ ceramic are 10.14  $\mu\text{C}/\text{cm}^2$  and 2.90 kV/cm. Similar to BCTZ, the BCTZ-Cu and BCTZ-Fe ceramics showed slim and saturated loops. The ferroelectric properties of the

BCTZ-Cu ceramic were better than the BCTZ ceramic ( $P_r=12.64 \mu\text{C}/\text{cm}^2$  and  $E_c=2.47 \text{ kV}/\text{cm}$ ). In contrast, the BCTZ-Fe ceramic ferroelectric properties were degraded (Table 1). Unlike the BCTZ, BCTZ-Cu and BCTZ-Fe ceramics, the loop of the BCTZ-Cr ceramic becomes unsaturated which indicated a leakage current was produced ( $P_r=16.41 \mu\text{C}/\text{cm}^2$  and  $E_c=6.57 \text{ kV}/\text{cm}$ ). In this work, samples of the BCTZ modified with Cu-induced good dielectric and ferroelectric behavior. This behavior can be attributed to the well-developed microstructure and the highest density of this sample. The microstructure enhanced the domain variants while the trapping of space charges at the boundaries was reduced, which makes domain reorientation easier (Bongkarn *et al.*, 2016; Jha *et al.*, 2009).

**Table 1** Data of density, transition temperatures and electrical properties of BCTZ, BCTZ-Cu, BCTZ-Cr and BCTZ-Fe ceramics.

Sample	Density ( $\text{g}/\text{cm}^3$ )	Relative density (%)	$T_{O-T}$ ( $^{\circ}\text{C}$ )	$T_c$ ( $^{\circ}\text{C}$ )	$\epsilon_r$	$\tan \delta$ at $T_r$	$\epsilon_c$	$\tan \delta$ at $T_c$	$P_r$ ( $\mu\text{C}/\text{cm}^2$ )	$E_c$ ( $\text{kV}/\text{cm}$ )
BCTZ	5.71	96.95	36	109	2964	0.087	11863	0.019	10.14	2.90
BCTZ-Cu	5.79	98.30	34	104	2951	0.017	12514	0.017	12.64	2.47
BCTZ-Cr	5.61	95.25	36	104	1790	0.037	8984	0.014	16.41	6.57
BCTZ-Fe	5.69	96.60	-	78	3097	0.026	10097	0.042	8.42	4.41

## CONCLUSION

In this work, we investigated the effects of  $\text{CuO}$ ,  $\text{Cr}_2\text{O}_3$  and  $\text{Fe}_2\text{O}_3$  doping on the phase formation, microstructure and electrical properties of BCTZ ceramics fabricated by the solid state reaction combustion technique. A pure perovskite phase and a morphotropic phase boundary between the orthorhombic and tetragonal phase were found in all samples. Compared with BCTZ ceramics, BCTZ-Cu and BCTZ-Cr ceramics exhibited a larger grain size while BCTZ-Fe showed a smaller grain size. Doping of Cu can improve the density and microstructure of BCTZ ceramics, caused by the presence of oxygen vacancies that helps mass transport during the sintering process. The BCTZ-Cu ceramic demonstrated a good morphology, the highest density ( $5.79 \text{ g}/\text{cm}^3$ ), the highest maximum dielectric constant ( $\epsilon_c=12500$ ) and good ferroelectric properties ( $P_r=12.6 \mu\text{C}/\text{cm}^2$  and  $E_c=2.5 \text{ kV}/\text{cm}$ ). All the results of the morphology, density, electrical and ferroelectric are consistent with each other.



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