Hue University Journal of Science: Natural Science
Vol. 129, No. 1D, 77–82, 2020

pISSN 1859-1388
eISSN 2615-9678

FACTORS AFFECTING CALCINING TEMPERATURES OF BZT–BCT CERAMICS

Bui Thi Ngoc Anh[1], Phạm Thi Thanh Minh[2], Le Tran Uyen Tu[3], Dung Thi Hoai Trang[3], Le Thi Lien Phuong[3], Vo Thanh Tung[3*]

[1] Tran Binh Trong high school, Phu Hoa, Phu Yen, Vietnam
[2] Hung Vuong Gifted High School, 48 Hung Vuong St., Pleiku, Gia Lai, Vietnam
[3] Department of Physics, University of Sciences, Hue University, 77 Nguyen Hue St., Hue, Vietnam

* Correspondence to Vo Thanh Tung <vttung@hueuni.edu.vn>

(*Received: 10 April 2020; Accepted: 13 June 2020*)

Abstract. Piezoelectric ceramic $0.48Ba[Zr_{0.2}Ti_{0.8}]O_3 - 0.52[Ba_{0.7}Ca_{0.3}]TiO_3$ (BZT–BCT) with nanostructure was manufactured with traditional ceramic technology. The nanostructure and the sintering aid reduce the calcining temperature from 1250 to 1170 °C and the sintering temperature from 1450 to 1350 °C. The piezoelectric properties of BZT–BCT at the optimal calcining and sintering temperature are discussed in detail.

Keywords: BZT–BCT, nanostructure, calcining temperature, sintering temperature

1 Introduction

It is well known that lead zirconate titanate (PZT) based ceramics have widely been used for piezoelectric applications because of their excellent piezoelectric behavior. Nevertheless, they are globally restricted due to the toxic lead oxide evaporating to the environment during preparation. With the recent growing demand for global environmental and human health protection, numerous lead-free ceramics have been systematically studied to replace lead-based ceramics [1, 2].

In 2009, alternating A or/and B sites in perovskite $BaTiO_3$, Liu and Ren established a new lead-free ferroelectric system $Ba(Zr_{0.2}Ti_{0.8})O_3 - x(Ba_{0.7}Ca_{0.3})TiO_3$ (abbreviated as BZT–BCT) that possesses excellent piezoelectricity (d_{33} = 620 pC/N at x = 50 composition) [3]. Since then, the BZT–BCT materials have been widely studied [4-7] It is noted that $BaTiO_3$-based ceramics are usually sintered at a very high temperature to obtain desired properties [6-8], which causes various difficulties in the preparation and application of these materials. It is well-known that there exist several methods for reducing the sintering temperature, such as the use of nanostructured raw materials and sintering aids [9-11].

In this paper, we study, in detail, the influence of the nanostructure of raw materials and the sintering aid CuO on the calcining and sintering temperature of BZT–BCT ceramics. The piezoelectric properties of BZT–BCT at the optimal calcining and sintering temperature are addressed.

2 Experimental

To select thermal parameters for the preparation of the solid solution, we analyzed the TGA-dTG curves for the BZT–BCT system (Fig. 1).

DOI: 10.26459/hueuni-jns.v129i1D.5769

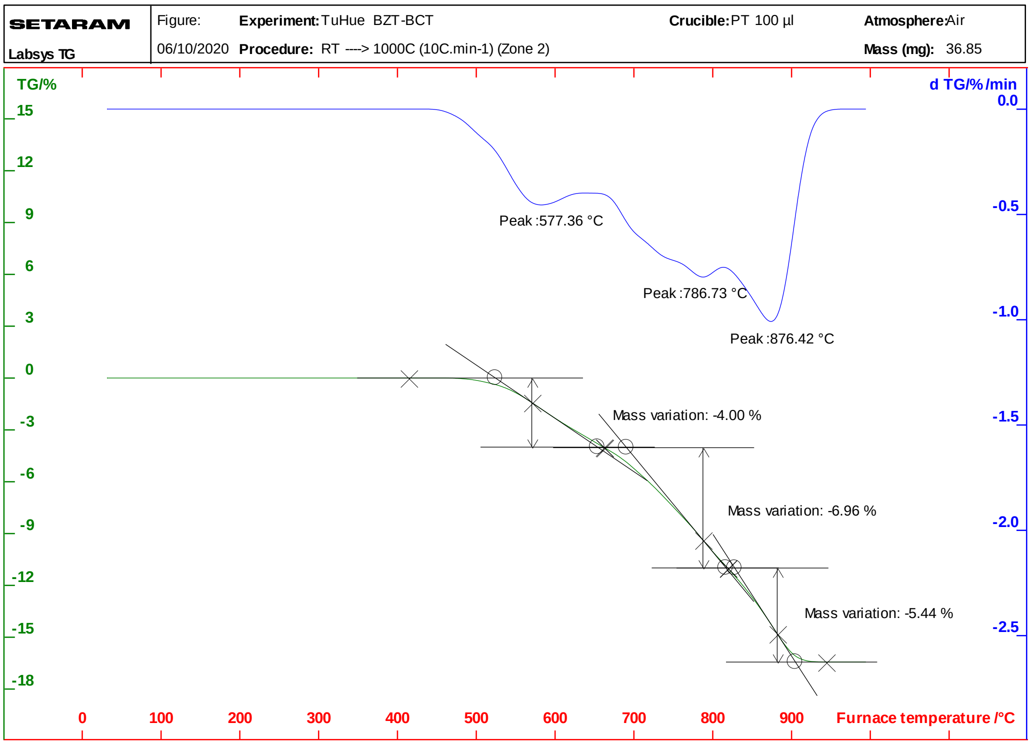

Fig. 1. TGA-dTG curves of BZT–BCT ceramics

The TGA-dTG curves recorded at a heating rate of 10 °C/min in the air for an equimolar mixture in the stoichiometric proportion of BZT–BCT composition are displayed in Fig. 1. Two distinct weight losses on the TG curve correspond to two endothermic peaks in the dTG curve. The first weight loss occurs around 577 °C, and the second locates at 876 °C. In principle, a solid-phase reaction occurs completely to form BZT–BCT solid solution at the second endothermic peak (corresponding to the highest weight loss in the investigated temperature region). This means that the temperature for calcination around 850 °C was chosen. However, the initial mass of the mixture in the stoichiometric proportion, used for recording TGA–dTG curves, was very small compared with the amount of the raw materials in our work; thus, the calcining temperature was 250–300 °C higher than the temperature corresponding to the endothermic peak, i.e., 1100–1200 °C.

From the thermal analysis, the conventional ceramics fabrication technique was used to prepare lead-free ceramics BZT–BCT doped with CuO nanoparticles (abbreviated as BZT- BCT + *y*CuO, where *y* is the content of CuO in wt %, *y* = 0.15). The raw materials with nanostructure and high purity (>99.9%) are $BaCO_3$, $CaCO_3$, ZrO_2, TiO_2 (Merck). They were weighed and mixed in a ball milling machine for 3 h, with ethanol as a medium. The obtained powder was annealed at 1150, 1170, and 1200 °C for 3 h. The obtained annealed powder was milled again in ethanol for 2.5 h and then pressed into desired-shape specimens by pressing uniaxially under a pressure of 100 MPa. To evaluate the effect of CuO on BZT–BCT ceramic, the obtained annealed powder was milled with CuO in ethanol and pressed into desired-shape specimens. Sintering was carried out at 1320, 1350, and 1380 °C for 2.5 h. The crystalline structure of the sintered ceramics was investigated with X-ray diffraction (XRD, D8-Advanced, BRUKER AXS). The surface of the sintered samples was processed and cleaned ultrasonically. Then, scanning electron microscopic (SEM) images were taken on a Nova

pISSN 1859-1388
eISSN 2615-9678

NanoSEM 450-FEI. The specimens were covered with silver paste on both sides and fired at 450 °C for 30 minutes. To study piezoelectric properties, the specimens were polled in a silicon oil bath at 30 °C by applying a DC electric field of 1.7 kV/mm for 60 minutes. Main piezoelectric parameters were calculated with a resonance method (HIOKI 3532) and all formulas met the IEEE standards for piezoelectric ceramics characterization.

3 Results and discussions

The XRD diagram of BZT–BCT ceramics calcined at 1150, 1170, and 1200 °C are depicted in Fig. 2. At 1150 and 1200 °C, the material system exists in two phases. At 1170 °C, the ceramic exhibits a single phase structure of perovskite ABO_3, and no secondary phase is observed in the investigated range. At this temperature, the component ratio of 0.48BZT is significantly higher. Compared with previous studies [5, 8], the calcined temperature of BZT–BCT ceramics reduces from 1250 to 1170 °C. Thus, it is reasonable to calcine the samples at 1170 °C. And we found that the raw materials with nanostructure affect the calcining temperature of this ceramic.

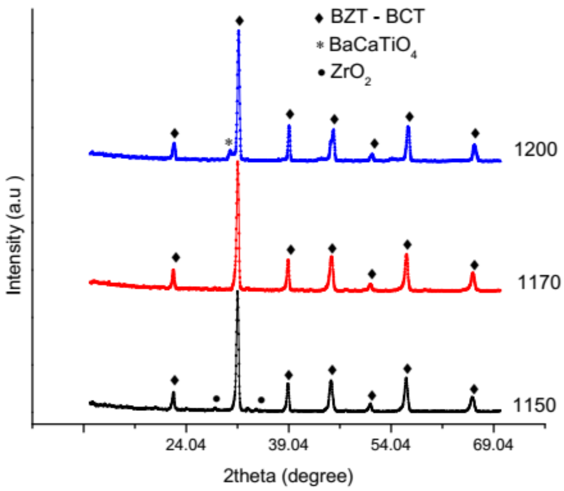

Fig. 2. XRD diagrams of BZT–BCT ceramics calcinated at 1150, 1170, and 1200 °C

After calcining at 1170 °C, the ceramics were sintered at 1320, 1350, and 1380 °C for 2.5 h. To determine the piezoelectric properties of the nanostructured BZT–BCT ceramics, we recorded the resonant vibration spectra of the samples at ambient temperature (Fig. 3). From the spectrum of radial resonance, we determined the electromechanical coupling factor (k_P) as a function of sintering temperature (Fig. 4).

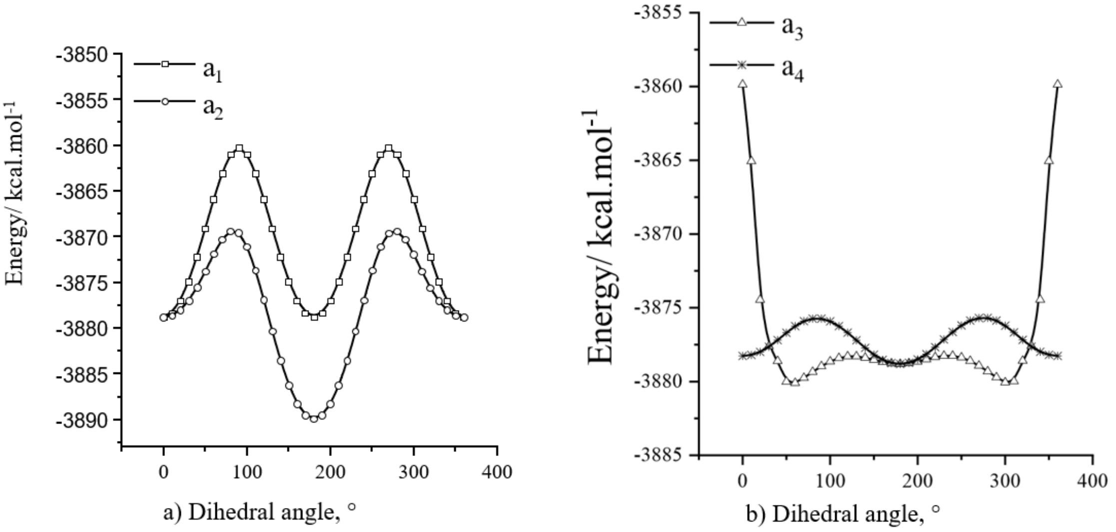

Fig. 3. Spectra of radial resonance of the BZT–BCT ceramics sintered at 1320, 1350, and 1380 °C

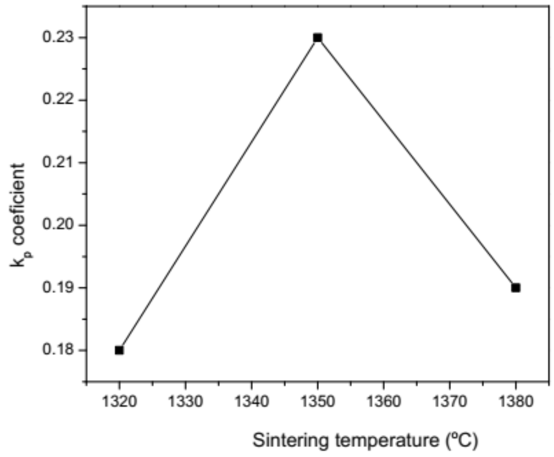

Fig. 4. Dependence of electromechanical coupling factor on sintering temperature of BZT–BCT ceramics

When the sintering temperature increases, the value of k_P also increases. The highest value for k_P (0.23) is obtained at 1350 °C. In general, the nanostructured BZT–BCT ceramics have a very low piezoelectric effect. Thus, the nanostructured raw material reduces the calcining temperature, but it does not affect the sintering temperature. This indicates that the phase of material forms after calcinating. Therefore, the nanostructured raw material affects the physical properties of the ceramics if it has a low sintering temperature.

To improve the piezoelectric properties, we use CuO as a sintering aid. Fig. 5 shows the density of the nanostructured BZT–BCT ceramics with 0.15 wt % CuO (BZT–BCT + 0.15 wt % CuO) sintered at 1320, 1350, and 1380 °C. The ceramic density reaches the highest value (5.60 g/cm^3) at 1350 °C.

To determine the piezoelectric properties of the BZT–BCT + 0.15 wt % CuO ceramics sintered at 1320, 1350, and 1380 °C, we measure the resonant vibration spectra of the samples at ambient temperature (Fig. 6).

From these resonant spectra, the piezoelectric parameters of samples were determined (Table 1 and Fig. 7).

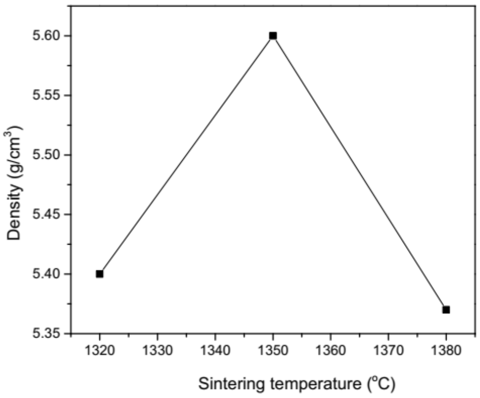

Fig. 5. Density of the BZT- BCT + 0.15 wt % CuO ceramics sintered at 1320, 1350, and 1380 °C

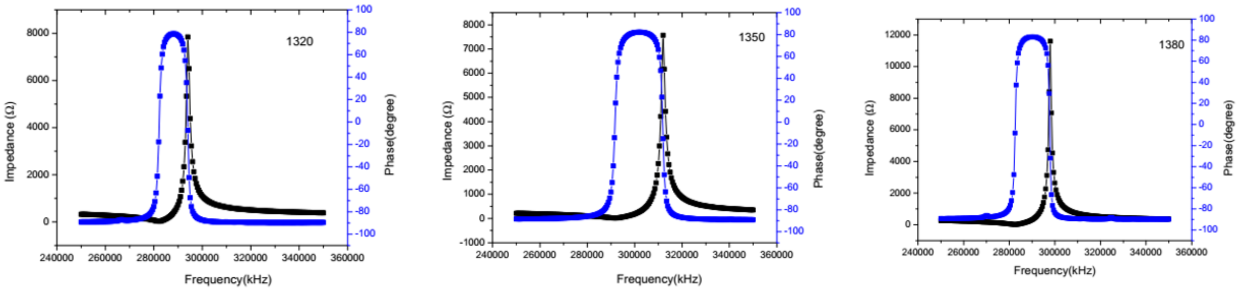

Fig. 6. Spectrum of radial resonance of the BZT–BCT + 0.15 wt % CuO ceramic sintered at 1320, 1350, and 1380 °C

Table 1. Piezoelectric parameters of BZT–BCT + 0.15 wt % CuO ceramic

Temperature (°C)	Z_{min} (Ω)	f_1(kHz)	f_2(kHz)	k_p	d_{33} (pC/N)
1320	37.1	283	294	0.30	253
1350	12.15	291.5	312	0.40	438
1380	12.37	282.5	2.98	0.35	332

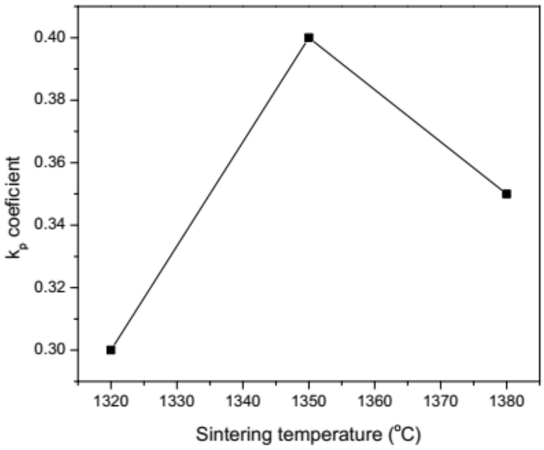

Fig. 7. Dependence of electromechanical coupling factor on sintering temperature BZT–BCT + 0.15 wt % CuO ceramics

Fig. 7 shows the electromechanical coupling factor of radial vibration mode (k_P) as the function of sintering temperature. The piezoelectric parameters of the BZT–BCT + 0.15 wt % CuO tend to enhance with sintering temperature. The largest values for k_P (0.40) and d_{33} (438 pC/N) are obtained at 1350 °C. The improvement of the electrical properties of the ceramics after adding CuO possibly results from the liquid phase formed during sintering that enhances the density and leads to the decrease of energy loss.

4 Conclusions

In this research, we found that raw materials with nanostructure decrease the calcined temperature of the BZT–BCT from 1250 to 1170 °C. However, the piezoelectric parameters are rather low. The addition of CuO enables to synthesize the BZT-BCT + 0.15 wt % CuO ceramics at a relatively low sintering temperature of 1350 °C with improved piezoelectric properties (d_{33} = 438 pC/N and k_P = 0.40). This lead-free BZT–BCT material could be potential for applications.

Funding statement

This work was carried out in the framework of the National Project in Physics Program until 2020 under No. ĐTĐLCN.10/18

References

1. Liu W, Ren X. Large Piezoelectric Effect in Pb-Free Ceramics. Physical Review Letters. 2009;103(25): 257602.
2. Xue D, Zhou Y, Bao H, Gao J, Zhou C, Ren X. Large piezoelectric effect in Pb-free Ba(Ti,Sn)O_3-x(Ba,Ca)TiO_3 ceramics. Applied Physics Letters. 2011;99(12):12290.
3. Damjanovic D, Biancoli A, Batooli L, Vahabzadeh A, and Trodahl J. Elastic, dielectric, and piezoelectric anomalies and Raman spectroscopy of 0.5Ba($Ti_{0.8}Zr_{0.2}$)O_3 - 0.5($Ba_{0.7}Ca_{0.3}$)TiO_3. Applied Physics Letters. 2012;100(19):192907.
4. Wu J. Advances in Lead-Free Piezoelectric Materials. Singapore: Springer; 2018. 522 p.
5. Tuan DA, Tinh NT, Tung VT, Van Chuong T. Ferroelectric and Piezoelectric Properties of Lead-Free BCT-xBZT Solid Solutions. Materials Transactions. 2015;56(9):1370-1373.
6. Wang P, Li Y, Lu Y. Enhanced piezoelectric properties of ($Ba_{0.85}Ca_{0.15}$)($Ti_{0.9}Zr_{0.1}$)O_3 lead-free ceramics by optimizing calcination and sintering temperature. Journal of the European Ceramic Society. 2011;31(11):2005-2012.
7. Su S, Zuo R, Lu S, Xu Z, Wang X, Li L. Poling dependence and stability of piezoelectric properties of Ba($Zr_{0.2}Ti_{0.8}$)O_3-($Ba_{0.7}Ca_{0.3}$)TiO_3 ceramics with huge piezoelectric coefficients. Current Applied Physics. 2011 05;11(3):S120-S123.
8. Tuan DA, Vuong LD, Tung VT, Tuan NN, Duong NT. Dielectric and ferroelectric characteristics of doped BZT-BCT ceramics sintered at low temperature. Journal of Ceramic Processing Research. 2018;19(1):32-36.
9. Le QTD, Truong VC, Do PA. The effect of TiO 2 nanotubes on the sintering behavior and properties of PZT ceramics. Advances in Natural Sciences: Nanoscience and Nanotechnology. 2011;2(2):025013.

10. Hayati R, Barzegar A, Mat. Microstructure and electrical properties of lead free potassium sodium niobate piezoceramics with nano ZnO additive. Materials Science and Engineering: B. 2010;172(2): 121-126

11. Tuan DA, Tung VT, Vuong LD, Yen NH, Tu LTU. Investigation of phase formation and poling conditions of lead-free $0.48Ba(Zr_{0.2}Ti_{0.8})O_3$–$0.52(Ba_{0.7}Ca_{0.3})TiO_3$ ceramic. Journal of Electronic Materials. 2018;47(10):6297-6301.