Phase characteristics, microstructure, and dielectric properties of $Ba_{0.7}Ca_{0.3}TiO_3$-$BaTiO_3$ ceramics

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Abstract

In this work, phase characteristics, microstructure, and dielectric properties of (100-x)$Ba_{0.7}Ca_{0.3}TiO_3$-(x)$BaTiO_3$ (BCT-BT) where x=0, 30, 50, 70, and 100 wt% were investigated. The ceramics were prepared using a conventional solid-state sintering technique. The optimized sintering temperatures were between 1,400 ^{o}C. The relative density values of all sintered ceramics were higher than 95%. X-ray diffraction patterns resulted confirmed the tetragonal structure of these ceramics, except BCT ceramic. BCT ceramic had a board dielectric peak; BT had a sharp dielectric peak. BCT-BT binary ceramic showed a sharp dielectric behavior. The composition *x*=70 wt% had maximum dielectric constant. These results suggested that the dielectric properties of BT and BCT could be modified using their binary ceramic, which made this material for dielectric devices.

Keywords: ceramics, dielectric, ferroelectric, piezoelectric

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Introduction

Piezoelectric material is one of the essential materials relevant and has been used in many different sectors such as actuators, flexible electronics, resonators, tactile sensors, energy harvesting, and medical sensors. The traditionally popular piezoelectric material is Lead zirconate titanate (PZT) because PZT has excellent properties, but PZT is composed of Pb as a toxic element (Liu, & Ren, 2009; Jaibana, Watcharapasorn, Yimnirun, Guo, & Bhalla, 2018; Jaiban et al., 2019; Yang et al., 2019;). Several researchers are pointing to a lead-free piezoelectric material for this problem due to the environmental issue of lead-based piezoelectric material, i.e., PZT. Among the lead-free piezoelectric material, barium titanate ($BaTiO_3$) is the most popular because it has good properties (Frattini, Loreto, Sanctis, & Benavidez, 2012).

Recently, many researchers have studied the research on lead-free materials; for example, the binary ceramic between $BaZr_{0.2}Ti_{0.8}O_3$ (BZT) and $(Ba_{0.7}Ca_{0.3})_{0.985}La_{0.1}TiO_3$ (BCLT). The BZT-BCLT ceramic system promoted attractive piezoelectric and dielectric properties (Liu, & Ren, 2009; Jaiban et al., 2019). This work became the introduction of binary ceramic aspects. Thus, we are interested in studying binary ceramic. We found that the binary system between $BaTiO_3$ (BT) and $Ba_{0.7}Ca_{0.3}TiO_3$ (BCT) has not been reported yet. Therefore, (1-x)BCT-(x)BT binary ceramic by solid-state sintering was studied. It should be noted that the difference between (1-x)BCT-(x)BT binary ceramic and $Ba_{1-x}Ca_xTiO_3$ ceramic is powder and ceramic preparation. In the case of (1-x)BCT-(x)BT binary ceramic, the powders of BCT and BT had been synthesized separately. Then, BCT and BT calcined powders were weighed following ratio, and the mixed powder was pressed into a green body and sintered in the last step. Meanwhile, in the other, the starting oxide was weighed following the $Ba_{1-x}Ca_xTiO_3$ formula at the first step. Then, the mixed powder was calcined and sintered in the last step. The pure ceramics of BCT and BT were also fabricated to compare with the binary sample. X-ray diffraction technique (XRD) investigated all ceramics' phases and crystal structures. Scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDS) was employed to observe the microstructure and chemical composition, respectively. The relationship between all ceramics' phases, microstructure, and dielectric properties will be discussed.

Methodology

The starting oxides were $BaCO_3$ (98.5%, Sigma-Aldrich), $CaCO_3$ (99.95%, Sigma-Aldrich), and TiO_2 (99%, Sigma-Aldrich). The oxides were weighed according to $Ba_{0.7}Ca_{0.3}TiO_3$ for BCT and $BaTiO_3$ for BT systems. All weighed powders were ball milled in ethanol for 12 hrs. After that, it was

dried to evaporate the ethanol by putting it in the oven for 24 hrs. The dried powders in a closed alumina crucible were calcined at 900 °C for 2 hrs with a 5 °C/min heating rate. After obtaining BCT and BT powders, the calcined powders were mixed in the following composition. $Ba_{0.91}Ca_{0.09}TiO_3$ was noted as (0.7)BT-(0.3)BCT (7:3). $Ba_{0.85}Ca_{0.15}TiO_3$ was noted as (0.5)BT-(0.5)BCT (5:5). $Ba_{0.79}Ca_{0.21}TiO_3$ was noted as (0.3)BT-(0.7)BCT (3:7). The (1-x)BCT-(x)BT powders were mixed in ethanol for 12 h. Then, the mixed powders were dried in the oven for 24 hrs.

For ceramic fabrication, the dried powders with different compositions were added with polyvinyl alcohol (PVA). The powders were pressed into pellets using a uniaxial press with 1 ton for 15 s. After that, the pellets were sintered in a closed alumina crucible. The first temperature was 500 °C for 1 hr to eliminate the PVA binder. The second step of sintering was at 1,400 °C for 4 hrs.

The density of ceramics was calculated from the ratio between mass and volume of the ceramic. For the characterization, X-ray diffraction (XRD) in a 2-theta range of 10 to 80° was used to identify the ceramic phase. The ceramic microstructure and chemical composition were observed by scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDS). Both sides of the pellets are coated with silver electrodes for dielectric measurement. The temperature dependence of dielectric permittivity and dielectric loss are performed by an LCR meter in a temperature range from room temperature to 200°C with a heating rate of 2°C/min at 1 kHz to 1 MHz. The overview of sample preparation and characterization is illustrated in (Figure 1).

Results and discussion

Bulk density values of all ceramics are shown in (Figure 2). The BCT had the lowest density, about 5.2 g/cm^3. The density values increased with the increase of BT. The BT had the highest density, about 6.2 g/cm^3. The relative density values of all ceramics were calculated from bulk density and theory density. The result revealed that the ceramics had a relative density higher than 95%. This confirmed that, upon the sintering temperature at 1,400 °C, it could produce the dense pellet of all ceramics.

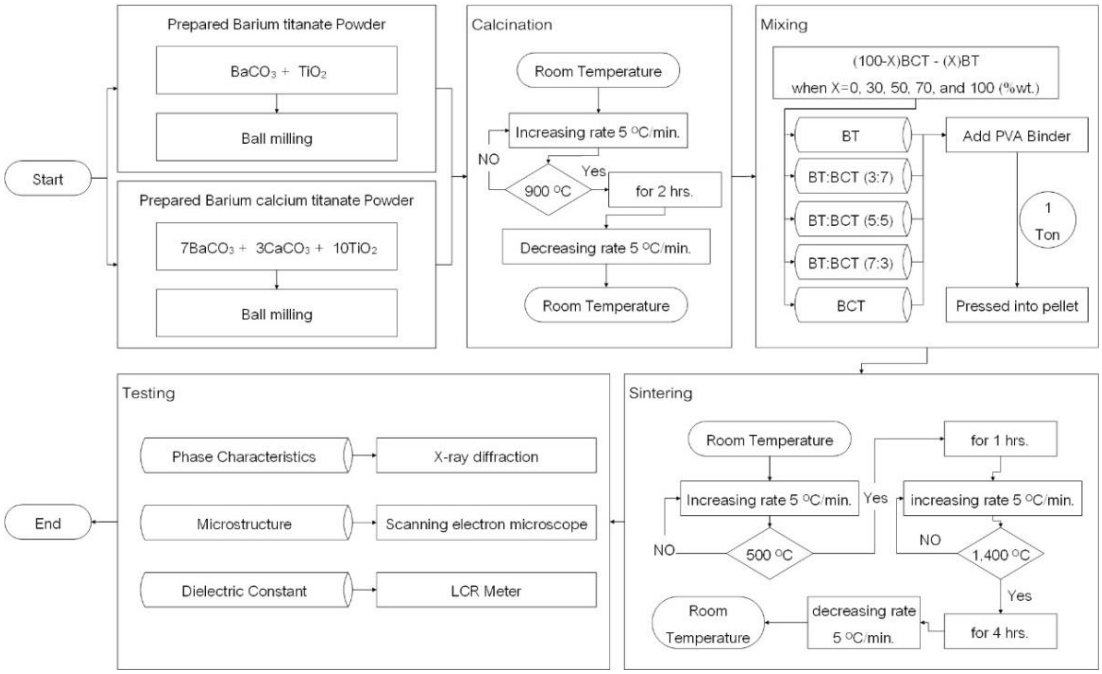

Figure 1 Experimental schematic diagram.

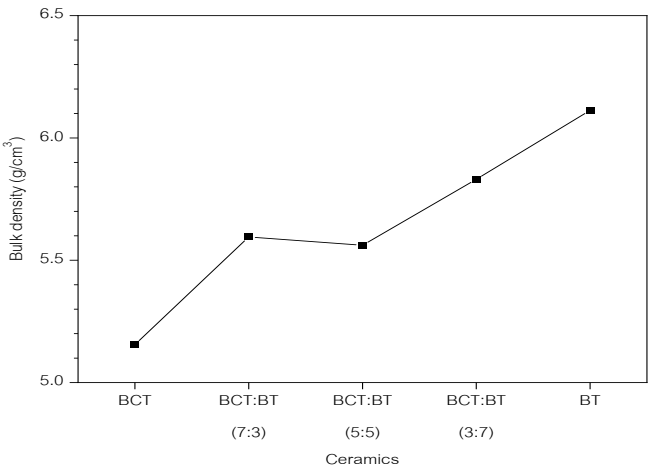

Figure 2 Density values of all ceramics.

X-ray diffraction results of all ceramics are shown in (Figure 3). As seen in (Figure 3a), the (110) peak existing at approximately 31.5° and the spilling peaks of (002) and (200) around 45° suggested a tetragonal structure in BT ceramic. However, there was the presence of the $BaCO_3$ secondary phase. This result indicated incomplete formation in the BT compound. In the case of BCT, it was found that the

ceramic had a binary phase between tetragonal and orthorhombic structures (Jaibana, Watcharapasorn, Yimnirun, Guo, & Bhalla, 2018). The secondary phase of $BaCO_3$ was still observed in BCT. However, the presence of a secondary phase in BCT did not affect its electrical properties, which had been reported in previous works (Jaibana, & Watcharapasorn, 2017). Interestingly, when BCT was added, the XRD pattern of doped BT became similar to BCT. However, there was no orthorhombic phase in BT-BCT ceramics. The BT:BCT (3:7) ceramic had no secondary phase.

The magnification of 2θ range from 26-36° is given in (Figure 3b). The results revealed a shift of XRD peaks to a higher diffraction angle with an increase in BCT content. This shift was due to the reduction of crystal structure volume. The substitution of smaller ion of Ca (ionic radius ~1.34 Å) to the larger ion of Ba (ionic radius ~1.61 Å) at the A-site of BT perovskite ceramic induced such reduction. This evidence confirmed that Ca ions diffused BT by substitution at Ba ions. This result was in agreement with previous works (Pullar et al., 2009).

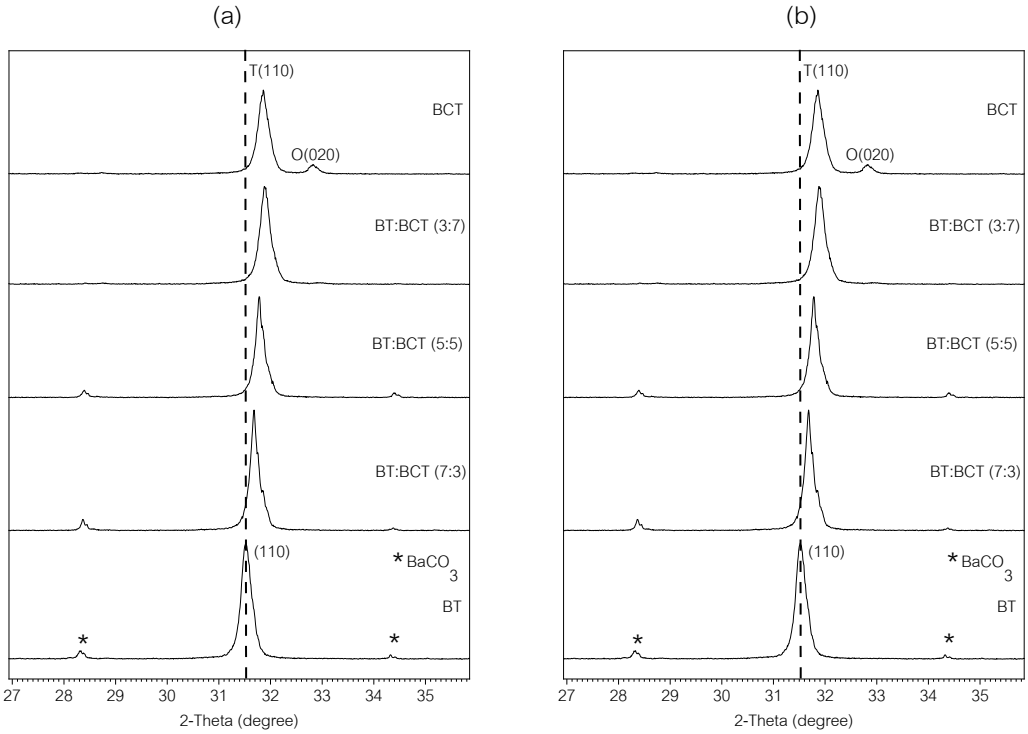

Figure 3 XRD patterns of all ceramics when (a) 2θ = 10 – 80°, and (b) 2θ = 26 - 36°.

The fracture surface of all samples was observed using SEM, as shown in (Figure 4). The figure shows that it was difficult to mention these ceramics' grain size, except BT. The BT showed clear grains on the fracture surface. The BT grain size was ranged estimated from 4 to 7 μm. The result suggested a strong grain, which produced intergranular fracture; the others showed transgranular facture.

(Figure 5) shows the EDS mapping images of all ceramics. BCT ceramic was composed of barium (Ba), calcium (Ca), titanium (Ti), and oxygen (O). The composition of BCT accompanied these elements. Regarding the doped ceramics, it was found the doped ceramics were composed of Ba, Ca, Ti, and O. These results supported the absence of other elements, which accompanied the XRD result.

The spectra of the dielectric constant and dielectric loss values at 10 kHz are illustrated in (Figure 6a-6e). All ceramics showed a phase transition temperature of around 160 °C. It was observed that the dielectric peak of BCT was diffuse. This was because of the inhomogeneous contribution of this ceramic. The others showed a sharp dielectric peak, which reflected a normal ferroelectric material.

The comparison of dielectric constant and dielectric loss of all ceramics are shown in (Figure 7a-7b), respectively. It could be seen that the ceramic BCT:BT at 7:3 had a maximum dielectric constant of almost 3500 at 160 °C. BT ceramic had the maximum dielectric constant value around 3000; meanwhile, BCT had the maximum dielectric constant value of around 1500.

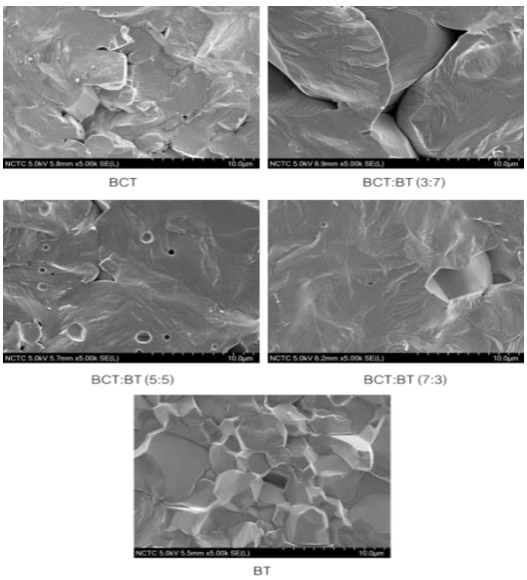

Figure 4 Microstructural images of all ceramics.

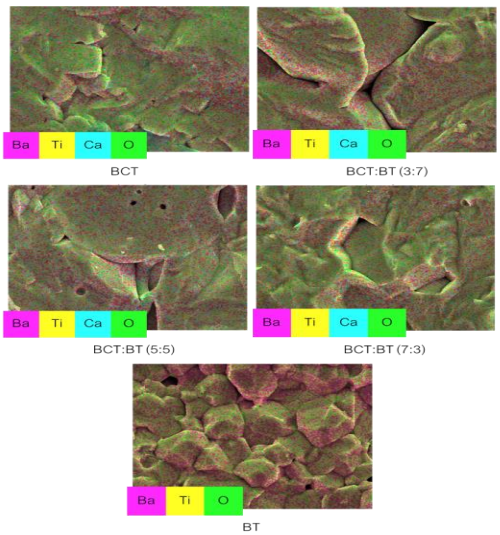

Figure 5 EDS mapping images of all ceramics.

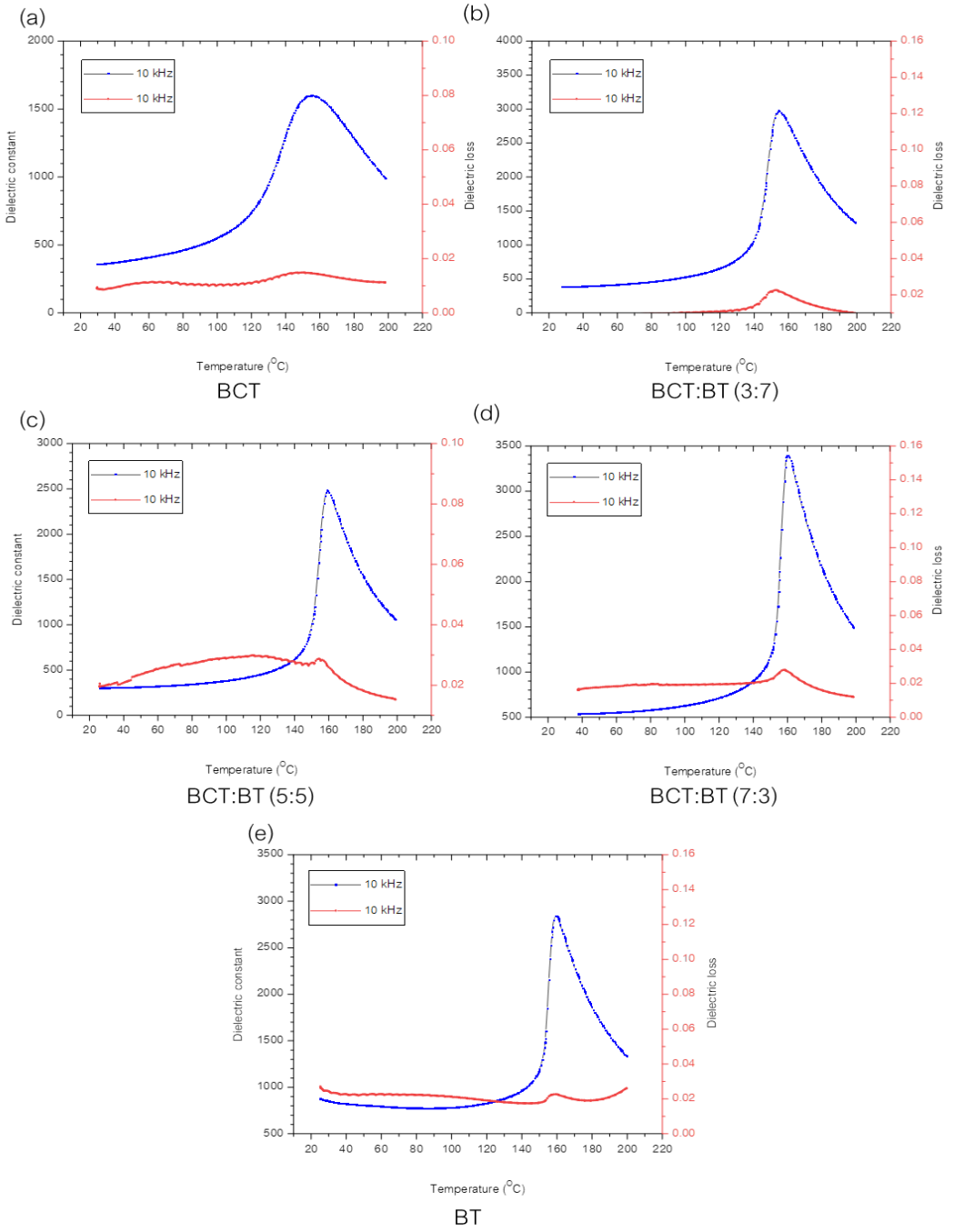

Figure 6 (a), (b), (c), (d), and (e) are dielectric properties as a function of temperature at 10 kHz of BCT, BCT:BT (3:7), BCT:BT (5:5), BCT:BT (7:3), and BT, respectively.

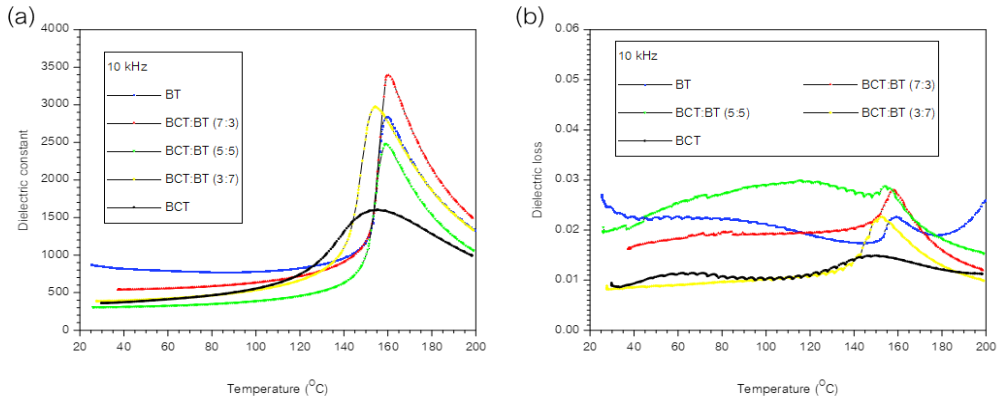

Figure 7 (a) and (b) compare dielectric constant and dielectric loss, respectively.

Regarding the Curie temperature (T_c) of BT in our work, it was about 160 °C. This value differed from other BT ceramics, which had about 120 °C - 130 °C. The factor that shifted T_c from 120 °C to 160 °C might be the formation of the $BaCO_3$ secondary phase. $BaCO_3$ formation induced Ba deficiency in BT stoichiometric ceramic, which was similar to Ba vacancy in the ceramic. The increase of T_c due to the generation of Ba vacancy had been suggested in Jonghe, & Rahaman (2003). The enhancement of T_c to high temperature made BT a promising candidate for high-temperature dielectric materials. Besides high T_c, the T_c of BT depended on BCT content. The BT ceramic had T_c of about 160 °C; the BCT ceramic had about 150 °C. The (1-x)BCT-(x)BT binary ceramic showed the variation of T_c in such temperature range. This behavior was explained by the Ca ions going into the A sites of Ba in the perovskite structure (Pullar et al., 2009). The lowest dielectric values of BCT were attributed to its diffuse dielectric behavior. The result here suggested that the combination between BT and BCT could improve the dielectric properties of BT.

Conclusion

This study successfully fabricated BT, BCT, and BCT-BT binary ceramics using a solid-state sintering technique. The $BaCO_3$ secondary phase was observed in the ceramics. BT ceramic had a tetragonal structure; meanwhile, BCT had a binary phase between orthorhombic and tetragonal structures. The SEM and EDS results confirmed that all ceramics were composed Ba, Ca, Ti, and O elements. The BCT:BT (7:3) had a maximum dielectric constant of almost 3500 at 160 °C. The formation of $BaCO_3$ increased the T_c of BT to 160 °C. The substitution of Ca at Ba ions reduced crystal

structure volume and changed T_c of BCT-BT binary ceramics. The result here indicated that their binary system could improve the dielectric properties of the BT and BCT pure systems.

Acknowledgement

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