# Study on the Textured CaBi$_4$Ti$_4$O$_{15}$ Ceramics with Sc Modification

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**Abstract.** Sc$^{3+}$ doped textured lead-free ceramics of CaBi$_{4-x}$Sc$_x$Ti$_4$O$_{15}$ (CBScT) were prepared by oriented consolidation of anisometric particle method with tape casting while the plate-like powders were produced by MMS method. The higher dielectric constant and lower dielectric loss were obtained as the $x$=0.2. The relationship between dielectric and ferroelectric properties were discussed. Within the optimal Sc doping content, the measured $\varepsilon_r$, $tan\delta$, $Pr$ and $T_C$ are 165, 1.8%, 8 μC/cm$^2$ and 700 °C, repectively.

## 1 Introduction

With the growing attention on lead-free ceramics materials development, the Aurivillius family of bismuth layer-structured ferroelectric (BLSF) ceramics caught more and more attentions for their relatively high Curie temperatures, low dielectric constants, low aging rate, strong anisotropic characters, high electromechanical coupling factors, low temperature coefficient of resonant frequency and none Pb content in the compositions [1-4]. Therefore, BLSF ceramics were regarded as one of potential candidates to substitute lead-based ones for their great potential applications in sensing technology of piezoelectric devices under high temperature, such as filters, sensors, and oscillators [5,6]. The generally chemical formula of BLSF is usually symbolized as $(Bi_2O_2)^{2+}(A_{m-1}B_mO_{3m+1})^{2-}$, where A stands for element with large ionic radius (such as K$^+$, Ca$^{2+}$ and Bi$^{3+}$), B indicates a transition element with small ionic radius (such as Fe$^{3+}$, Ti$^{4+}$, Nb$^{5+}$ and W$^{6+}$). The basic structure illustration of BLSF is presented in Figure 1. Electrically, the piezoelectric properties of BLSFs are strongly dependent on the value of $m$ and the pseudo-perovskite blocks between the $(Bi_2O_2)^{2+}$ layers [7-9].

Calcium bismuth titanate, CaBi$_4$Ti$_4$O$_{15}$ (CBT) is a typical member of BLSF family with m=4, its Curie temperature is about up to 790 °C and low dielectric loss, indicating promising candidate for high temperature piezoelectric applications However, CBT ceramics are greatly difficult to be poled due to the relatively high coercive fields. Thus CBT ceramics exhibit a piezoelectric property of only 3~7 pC/N [10]. To overcome these disadvantages, lots of research works about CBT ceramics was focused on enhancing its properties by rare-earth element doping and grain orientation techniques [11,12], etc. Based on previous studies, A-site substitution reveals more effective than B-site substitution because the cations in B-site have the similar in size and hardly make a major contribution to the polarization process [13].

In this work, Sc modified CBT textured ceramics of Ca(Bi$_{1-x}$Sc$_x$)$_4$Ti$_4$O$_{15}$ (CBScT-$x$, $x$=0, 0.1, 0.2, 0.3) were prepared by orientating consolidation of anisometric particles (OCAP) method via tape casting. Tape casting is capable of fabricating flexible and low-cost thick films with widest thickness range indicating the great advantage in forming large-area, thin and flat ceramic parts. In addition, Sc was selected for its great doping effects in high-temperature piezoelectric ceramics especially Bi-based compositions. Here, plated-like CBScT particles were firstly prepared by NaCl-KCl molten salt synthesis (MSS) method [14].
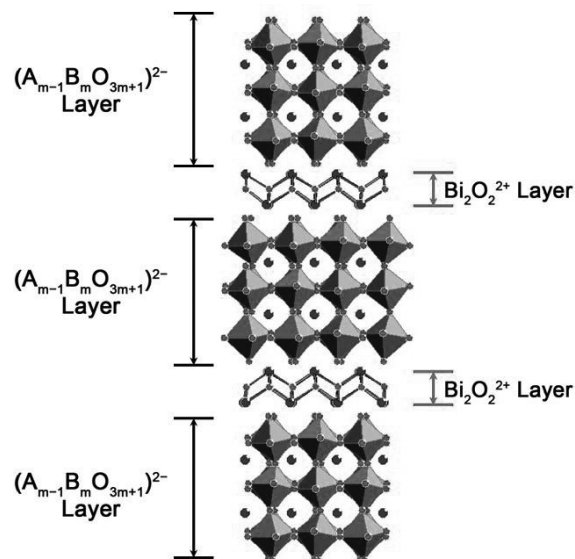


**Figure 1.** Illustration for the BLSF structure of $(Bi_2O_2)^{2+}(A_{m-1}B_mO_{3m+1})^{2-}$.

## 2 Experimental procedure

The Ca(Bi$_{1-x}$Sc$_x$)$_4$Ti$_4$O$_{15}$ (CBScT) ceramic samples with were prepared by molten salt synthesis molten salt synthesis method. Analytical grades powders of CaCO$_3$, Bi$_2$O$_3$, Sc$_2$O$_3$, TiO$_2$, KCl and NaCl were used as raw materials. The oxides were blended and ball milled for 24 h, then the mixture was dried and calcined at 1000 °C for 2~4 hours in a sealed alumina crucible. The synthetic product was washed with hot distilled water to remove the salts until no chloride ion was detected by AgNO$_3$ reagent. The obtained plated-like powders were then mixed with solvent, binder, plasticizer and ball milled for another 12 hours to form fine casting slurry. The binder and plasticizer were polyvinyl butyral (PVB), dibutyl phthalate (DBP) and polyethylene glycol (PEG), respectively. The slurry was degassed under vacuum device and tape-casted on a plate glass surface. After

being dried in air for about 72 h, the green sheets were cut and laminated into disks of 12 mm in diameter at 100 MPa to form compacts. Following an organic additives heating process at 650 ℃ for 24 h, the pressed tablets were finally sintered at 1100-1200 ℃ in air for 3 hours and then cooled down to room temperature freely.

Finally, the ceramics were polished and coated with sliver electrodes on both sides. The crystallographic phases of the prepared CBScT ceramics were characterized by X-ray diffraction (Rigaku D/Max 2200, Japan). The fracture surface morphology of the ceramics was observed by scanning electron microscopy (Hitachi S3400, Japan). Dielectric and ferroelectric properties were measured by a precision impedance analyzer (Agilent HP4294A, USA) and a ferroelectric measurement system (Radiant Premier II, USA), respectively.

# 3 Results and discussion

Figure 2 presented the morphology of CBScT powders produced by conventional solid state reaction method and molten salt synthesis method, respectively. Furthermore, the surface and fracture of the sintered textured ceramics were also illustrated. It is noted that the powders obtained by conventional solid state reaction tend to be regular ball-like shape while by MMS method were plate-like. Moreover with the time of reaction increasing, the planner area enlarged more and fitted the needs of orientating consolidation of anisometric particle. For 2 h in MMS reaction, the average size of the powder is about 2 μm, for 3 h the average size increased to 3 μm while the 4 h 5 μm. CBNT powders produced by MMS for 4 h were selected for continuous casting process. For the ceramics the highly aligned grains can be observed indicating the enhanced electric porperties.

Figure 3 shows the XRD patterns of synthesized $Ca(Bi_{1-x}Sc_x)_4Ti_4O_{15}$ ($x$=0, 0.1, 0.2, 0.3) (abbreviated as CBT, CBScT-1, CBScT-2 and CBScT-3 later) ceramics, respectively. It is obvious that all the ceramics with different compostions are crystallized into pure perovskite structure without any second phases. In addition, the relevant peaks become stronger indicating excellent crystallization along the optimized orientation. Besides, the Sc doping were not able to change the crystal structure indicating no great distortion happened with the Sc content doping into the CBT system.

Figure 4 exhibits the dielectric constant ($\varepsilon_r$) and dielectric loss ($tan\delta$) as a function of the Sc content for $Ca(Bi_{1-x}Sc_x)_4Ti_4O_{15}$ ceramics. It can be seen that the value of $\varepsilon_r$ increases initially to the highest value of 165, when x=0.2, and then decrease dramtically with the further increase of the Sc content. The tendency for $tan\delta$ is oppsite. The loss value decreases initially and reached the lowest point of 1.8% when x=0.2, and then increases with the Sc content increasing. Meanwhile, the optimal doping content was obtained based on the dielectric measurements, at x=0.2 with the $\varepsilon_r$, $tan\delta$ of 165 and 1.8% at 1 kHz, respectively.
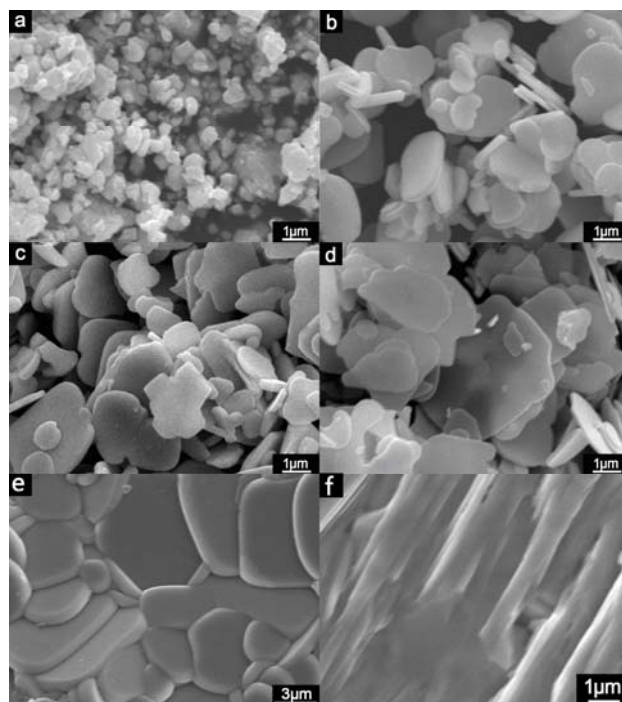


**Figure 2.** SEM of CBScT powders produced by (a) conventional method for 2 h, (b) MMS for 2 h, (c) MMS for 3 h, (d) MMS for 4 h, and ceramics on (e) surface, (f) fracture.
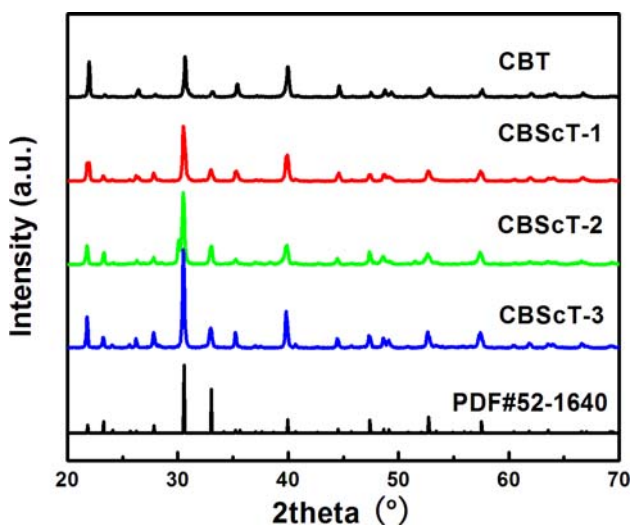


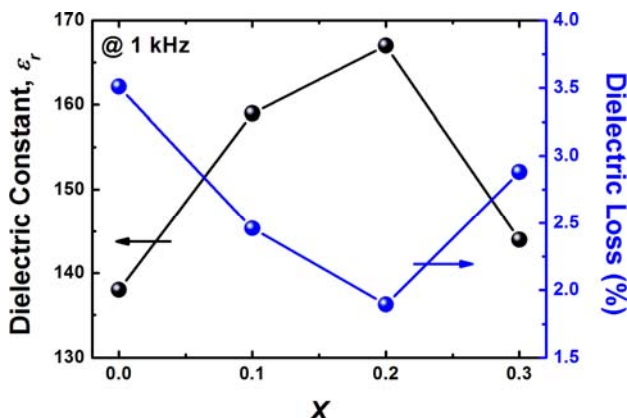**Figure 3.** XRD patterns of textured CBScT ceramics.



**Figure 4.** Dielectric properties of textured CBScT ceramics as the function of Sc content at 1 kHz.
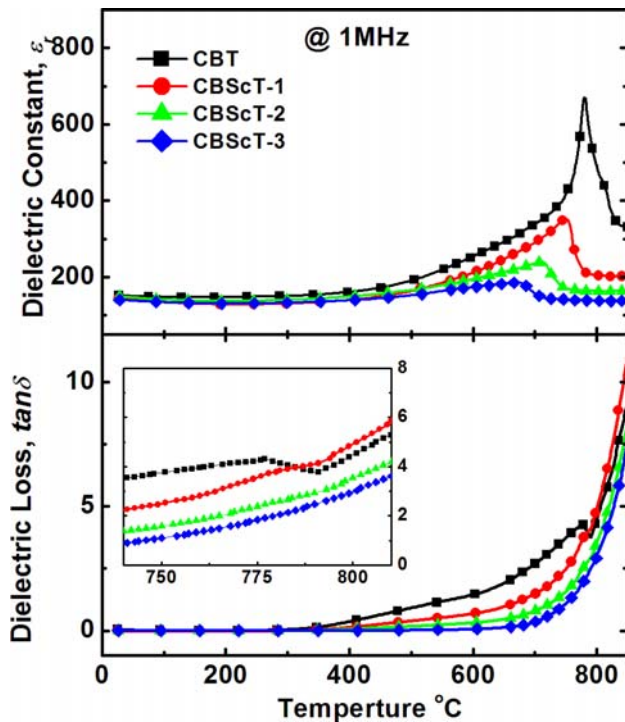
**Figure 5.** Temperature dependence on $\varepsilon_r$ and $tan\delta$ of textured CBScT ceramics.

The temperature dependence of $\varepsilon_r$ and $tan\delta$ measured at 1 MHz was shown in Figure 5. The dielectric maximums are observed in all compositions, reflecting the ferroelectric-paraelectric phase tranformation. The $T_C$ determined by the temperature at the dielectric peak ranges from 650 - 790 $^o$C. The $T_C$ is about 700 $^o$C for $x$=0.2, which is about 300 $^o$C higher than that of hard PZT ceramics. According to the results, it is obvious that with the increase of Sc doping content, the $T_C$ decreases slowly. From pure CBT to 0.1 Sc doping composition, the $T_C$ decreases about 50 $^o$C. With further 10 at.% Sc doping to $x$=0.2, another ~50 $^o$C decrease in $T_C$ was obtained. Same situation was also observed in 0.3 Sc composition. Thus, an ordinary conclusion about every 10 at.% Sc doping in Bi-site of CBT ceramics decreasing 50 $^o$C in $T_C$ can be deduced. In addition, with the increasing Sc content in CBScT ceramics, peaks reveal a broden trend phenomenon which will be useful for widening the temperature region application. For the dielectric loss, the transition peak can not be observed in Sc doping compositions. And the high temperature stability was enhanced by the Sc doping. However, via Sc modification, it effects less in reducing the loss in high temperature (over 800 $^o$C) region.

Figure 6 shows the *P-E* loops of un-poled Ca(Bi$_{1-x}$Sc$_x$)$_4$Ti$_4$O$_{15}$ ceramics measured at the elastic field of 10 kV/mm. The obtained polarization of specimens increases initially, and then decreases with the further increasing of the Sc doping content. However, the value of $E_c$ for all specimens is about fixed at 6 kV/mm. It is found that the specimen near x=0.2 exhibits better ferroelectric properties in this system, whose $P_r$ is 8 μC/cm$^2$ nearly doubled the $P_r$ value in pure CBT composotion.
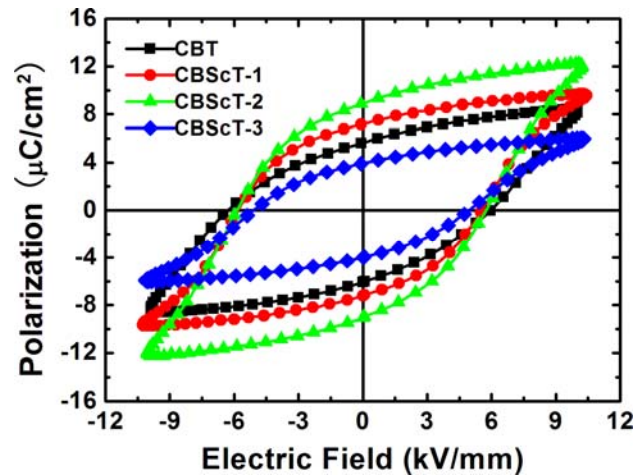


**Figure 6.** The polarization versus electric field hysteresis loops of un-poled textured CBScT ceramics at room temperature.

## 4 Conclusions

In summary, Sc$^{3+}$ doped textured CBT ceramics are prepared by the OCAP method via tape casting in this work. Plate-like powders with average size of 5 μm were obtained by MMS reaction method for 4 h. Highly aligned grains morphology was observed in the sintered ceramics. The optimal Sc doping content was deduced as x=0.2 based on the series measurement test on dielectric and ferroelectric properties.

Within the optimal Sc$^{3+}$ doping content, the measured $\varepsilon_r$, $tan\delta$, $Pr$ and $T_C$ are 165, 1.8%, 8 μC/cm$^2$ and 700 $^o$C, repectively, indicating the textured CBScT ceramics is possible to be used in the related high-temperature devices as a new kind of lead-free ferroelectric materials.

## References

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