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Featured Letter

# Super wide thermal stability and giant dielectric response of $(Ba_{1-x}Bi_{0.5x}Sr_{0.5x})(Ti_{1-x}Bi_{0.5x}Sn_{0.5x})O_3$ ceramics

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ABSTRACT

$(Ba_{1-x}Bi_{0.5x}Sr_{0.5x})(Ti_{1-x}Bi_{0.5x}Sn_{0.5x})O_3$ (BBSTBS, $0.02 \le x \le 0.1$) samples were prepared by a solid state reaction (SSR) method. The phase structure and dielectric properties of BBSTBS ceramics were investigated. X-ray diffraction results illustrated that BBSTBS could form a homogenous solid solution. Optimum properties with a stable $\varepsilon_r$ (~13,643–19,000), small $\Delta\varepsilon/\varepsilon_{25\,°C}$ values (±15%) over a broad temperature range from −61 °C to 210 °C and low tanδ (≤0.025) from −67 °C to 220 °C were obtained at $x = 0.06$.



## 1. Introduction

Nowadays, multilayer ceramic capacitors (MLCCs) are required to possess high dielectric constant and temperature stability in a wide working temperature range due to the application in harsh conditions [1]. Therefore, EIA (the Electronic Industries Association) X7R (−55 °C to 125 °C, $\Delta\varepsilon/\varepsilon_{25\,°C} \le \pm15\%$) and X8R (−55 °C to 150 °C, $\Delta\varepsilon/\varepsilon_{25\,°C} \le \pm15\%$) cannot meet the requirements [2,3]. So, it is significant to develop materials with excellent performances [4].

It is well known that the excellent dielectric properties of $BaTiO_3$ perovskite have been confirmed, and the compositions of most commercial ceramic dielectrics are based on $BaTiO_3$ [5]. Bismuth-based dielectric ceramics have been broadly studied for their relatively low sintering temperatures and high dielectric constants [6,7]. Therefore, a series of $BaTiO_3$-$BiMeO_3$ perovskite materials have been studied for the development in a broad temperature stability MLCCs, such as $BaTiO_3$-$Bi(Mg_{2/3}Nb_{1/3})O_3$ [8], $BaTiO_3$-$BiScO_3$ [9], $BaTiO_3$-$Bi(Mg_{0.5}Zr_{0.5})O_3$ [10], $BaTiO_3$-$Bi(Mg_{0.5}Ti_{0.5})O_3$ [11], etc. These materials showed good performances and some systems even exhibited outstanding properties with super-broad temperature stability. Therefore, $BaTiO_3$-based ceramics are worth to investigate in a broad temperature stability.

In our previous works, some $BaTiO_3$-based ceramics have been investigated, such as $BaTiO_3$-$Bi(Li_{1/3}Zr_{2/3})O_3$ [12] and $BaTiO_3$-$Bi(Mg_{2/3}Nb_{1/3})O_3$ [13]. And many researchers have reported that $SnO_2$ is an effective dopant to modify the temperature dependence of the permittivity for $BaTiO_3$-based ceramics [14,15]. Especially, $BaTiO_3$ solid solutions were formed in a large amount of Sn, which reduced the Curie temperature and did not broaden the phase transition [16]. In this work, $(Ba_{1-x}Bi_{0.5x}Sr_{0.5x})(Ti_{1-x}Bi_{0.5x}Sn_{0.5x})O_3$ composition was designed and prepared by the solid state reaction (SSR) method. Furthermore, the phase evaluation, microstructure and dielectric properties of ceramics were systematically studied.

## 2. Experimental

$(Ba_{1-x}Bi_{0.5x}Sr_{0.5x})(Ti_{1-x}Bi_{0.5x}Sn_{0.5x})O_3$ (BBSTBS, $0.02 \le x \le 0.1$) ceramic samples were prepared by the solid state reaction process using the starting materials of $BaCO_3$ (99%), $TiO_2$ (99%), $SrCO_3$ (99%), $Bi_2O_3$ (99%) and $SnO_2$ (99.5%). Stoichiometric proportions of BT ($BaTiO_3$) and BSBS [$(Bi_{0.5}Sr_{0.5})(Bi_{0.5}Sn_{0.5})O_3$] were weighed and milled in alcohol medium using zirconia balls for 4 h. After drying, the powders were calcined at 1100 °C and 750 °C for 4 h in air, respectively. Then, BBSTBS compositions were weighed and milled in alcohol medium using zirconia balls for 4 h. After drying, the powders were mixed with 5% polyvinyl alcohol (PVA) and pressed into pellets with 10 mm in diameter and 1.2 mm in thickness by uniaxial pressing at a pressure of 200 MPa. The pellets were embedded with the same calcined powders to avoid elements volatilization and sintered at different temperatures for 2 h in air (1280 °C–1380 °C), depending on the content of BSBS.

X-ray diffraction (XRD) patterns were recorded at room temperature using an X-ray diffractometer (XRD, Model X'Pert

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PRO; PANalytical, Almelo, the Netherland) with CuKα radiation (λ = 0.15406 nm) operated at 40 kV and 40 mA with a step size of 0.02°. The microstructural observation of the sintered samples was performed using a scanning electron microscopy (Model JSM6380-LV SEM, JEOL, Tokyo, Japan). Silver electrodes were coated on both sides of the pellets, and then fired at 700 °C for 30 min. Dielectric properties were measured using a precision impedance analyzer (Model E4980AL, Hewlett-Packard Co, Palo Alto, CA) with an applied voltage of 500 mV over 100 Hz–1 MHz from −120 °C to 250 °C at a heating rate of 2 °C/min.

## 3. Results and discussion

Fig. 1 shows the XRD patterns of $(Ba_{1-x}Bi_{0.5x}Sr_{0.5x})(Ti_{1-x}Bi_{0.5x}Sn_{0.5x})O_3$ ($0.02 \le x \le 0.1$) ceramics sintered at their optimized temperatures. In Fig. 1, no second phase was observed, indicating that a homogenous solid solution was formed with $(Bi_{0.5}\ Sr_{0.5})^{2.5+}$ entering the $Ba^{2+}$ sites and $(Bi_{0.5}Sn_{0.5})^{3.5+}$ occupying the $Ti^{4+}$ sites. As $0.02 \le x \le 0.1$, a tetragonal phase was clearly presented in all samples. To give a better illustration for the phase evolution, the Raman spectra in the frequency range of

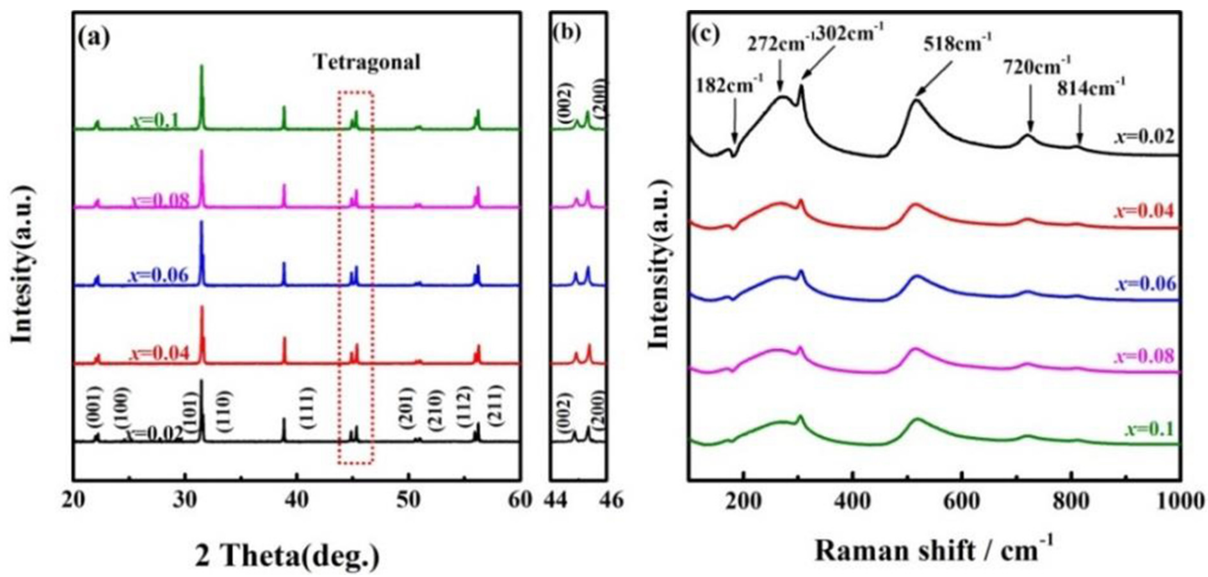


**Fig. 1.** (a) X-ray diffraction patterns of $(Ba_{1-x}Bi_{0.5x}Sr_{0.5x})(Ti_{1-x}Bi_{0.5x}Sn_{0.5x})O_3$ ($0.02 \le x \le 0.1$) ceramics, (b) The enlarged XRD patterns of ceramics in the range of 2θ from 44° to 46°, (c) Room temperature Raman spectra of $(Ba_{1-x}Bi_{0.5x}Sr_{0.5x})(Ti_{1-x}Bi_{0.5x}Sn_{0.5x})O_3$ ($0.02 \le x \le 0.1$) ceramics.

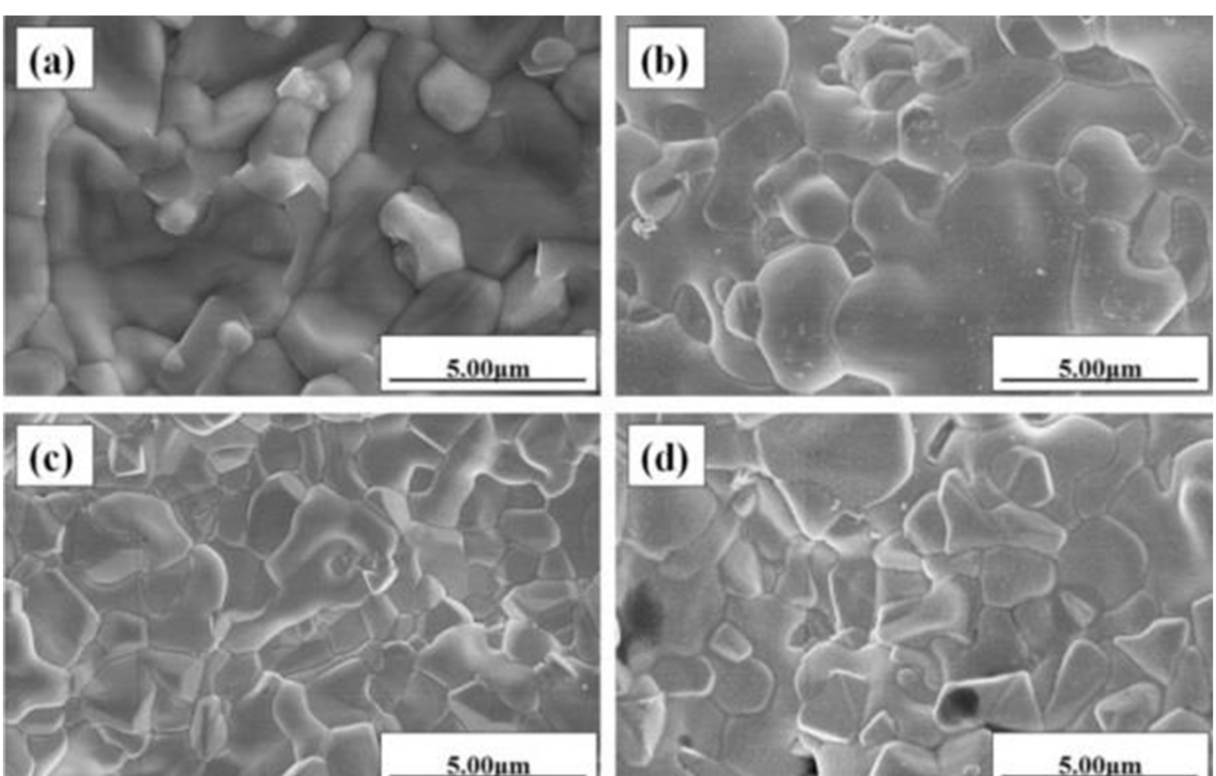


**Fig. 2.** SEM micrographs of $(Ba_{1-x}Bi_{0.5x}Sr_{0.5x})(Ti_{1-x}Bi_{0.5x}Sn_{0.5x})O_3$ ($0.02 \le x \le 0.1$) ceramic at their optimized sintered temperatures: (a) $x$ = 0.02, 1380 °C (b) $x$ = 0.04, 1360 °C (c) $x$ = 0.08, 1320 °C (d) $x$ = 0.1, 1280 °C.