

Improvement of dielectric loss of (Ba,Sr)(Ti,Zr)O₃ ferroelectrics for tunable devices

Jong-Yoon Ha^a, Ji-Won Choi^{a,*}, Chong-Yun Kang^a, Jin-Sang Kim^a,
Seok-Jin Yoon^a, Doo Jin Choi^b, Hyun-Jai Kim^a

^a Thin Film Materials Research Center, KIST, Seoul 130-650, South Korea

^b Department of Ceramic Eng., Yonsei University, Seoul 120-749, South Korea

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Abstract

(Ba_{0.6}Sr_{0.4})(Ti_{1-x}Zr_x)O₃ (0.05 ≤ *x* ≤ 0.3) ferroelectric materials have cubic perovskite structure and show paraelectric properties at room temperature. Curie point shifted to a negative value as increasing Zr content in (Ba_{0.6}Sr_{0.4})(Ti_{1-x}Zr_x)O₃ system. When Zr substituted 0.1 mol, the dielectric constant, dielectric loss, tunability, Curie point and FOM were 4500, 0.0005, 63%, −1.6 °C and 1260, respectively. This composition shows excellent microwave dielectric properties than those of (Ba_{0.6}Sr_{0.4})TiO₃ ferroelectrics, which are limelight materials for tunable devices such as varactors, phase shifters and frequency agile filters, etc.

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1. Introduction

Barium strontium titanate (BST) ferroelectric system with high dielectric constant is one of the attractive candidates for tunable high-frequency devices and dynamic random access memory (DRAM) applications. This property is very fascinating and has been used to develop devices operating in microwave such as phase shifters, frequency agile filters and tunable capacitors.¹ Dielectric materials for these devices should have higher dielectric constants, low dissipation factors and high tunability. There have been many studies in the development of the dielectric and tunable properties of ferroelectric BST materials because of its large field dependence permittivity and intrinsically fast field response. However, the high dielectric loss, especially in the microwave frequency range, limits its further development.^{2,3} In general, Ba_{0.6}Sr_{0.4}TiO₃ was chosen as the basic composition because of its good ferroelectric properties. However, this BST system has a little high dielectric loss even though having high tunability. For this reason, BST has a low figure of merit at microwave frequencies. It is well known that *T_c* and the dielectric properties of BaTiO₃ can be systematically changed in BaTiO₃ by chemical substitution of barium and/or

titanium by a wide variety of isovalent and aliovalent dopants.^{2,4} Recently, BaTiO₃-BaZrO₃-CaTiO₃ has been shown as an alternative to BST in fabrication of ceramic capacitors because Zr⁴⁺ is chemically more stable than Ti⁴⁺.^{5,6} In this paper, we have studied the effect of Zr⁴⁺ ion for substitution for Ti⁴⁺.

2. Experimental procedures

(Ba_{0.6}Sr_{0.4})(Ti_{1-x}Zr_x)O₃ (0.05 ≤ *x* ≤ 0.3) were synthesized by the conventional solid-state reaction method and the starting materials were SrCO₃, TiO₂, ZrO₂ (Aldrich, 99.9%), BaCO₃ (Aldrich, 99%). These were mixed in a ball mill with ethanol, then dried and calcined in an alumina crucible at 1000 °C for 6 h in air. The calcined powder was remilled with a 5 wt.% polyvinyl alcohol as a binder. Uniaxial pressing with 200 kg/cm² pressed the dried powders. These pellets with 18 mm diameter and 1–2 mm thick were sintered at 1450–1500 °C for 2 h in air. The heating and cooling rate were 5 °C/min. Silver paste electrodes were painted on both sides of sintered ceramic specimens for ferroelectric measurements. The bulk density was measured by the Archimedes method using distilled water as medium. X-ray diffraction (Cu Kα radiation D/MAX 2500, Rigaku) was carried out on powders for phase identification and lattice parameter measurements.

The capacitance and loss tan δ of the samples were measured using impedance analyzer (HP4192A) in the frequency range of

* Corresponding author.

E-mail address: jwchoi@kist.re.kr (J.-W. Choi).

1 kHz to 1 MHz. The capacitance also measured under various temperatures. The polarization-electric field loops were measured using a modified Saw-Tower circuit. Sintered ceramics were examined by powdered X-ray diffraction (XRD, Model Rint/Dmax 2500, Rigaku, Japan) analysis with Cu K α radiation. The microstructure of ferroelectric ceramics was investigated using a scanning electron microscope (SEM, Model S-4200, Hitachi, Japan).

3. Results and discussions

Fig. 1 shows X-ray diffraction spectra for $(\text{Ba}_{0.6}\text{Sr}_{0.4})(\text{Ti}_{1-x}\text{Zr}_x)\text{O}_3$ ($0.05 \leq x \leq 0.3$) ceramics sintered at 1500 °C for 2 h. The sintered $(\text{Ba}_{0.6}\text{Sr}_{0.4})(\text{Ti}_{1-x}\text{Zr}_x)\text{O}_3$ ceramics were single phase of cubic ($Pm3m$) structure. The (100) peak was shifted low angle with increasing Zr concentration. That means increasing the lattice parameter of $(\text{Ba}_{0.6}\text{Sr}_{0.4})(\text{Ti}_{1-x}\text{Zr}_x)\text{O}_3$ ceramics from 3.9686 to 4.032 Å. It is expected that the increase of lattice parameter by substitution of Sn occur because a slightly larger Zr^{4+} ion (0.72 Å) is incorporated to a B-site Ti^{4+} with slightly smaller ionic radius (0.609 Å) (Table 1).

The bulk density of $(\text{Ba}_{0.6}\text{Sr}_{0.4})(\text{Ti}_{1-x}\text{Zr}_x)\text{O}_3$ ceramics sintered at 1450–1500 °C for 2 h as a function of x is shown in Fig. 2. The bulk density decreased from 5.61 to 5.41 g/cm³ with increasing Zr concentration from 0.05 to 0.3 mol. The relative density of $(\text{Ba}_{0.6}\text{Sr}_{0.4})(\text{Ti}_{1-x}\text{Zr}_x)\text{O}_3$ ($0.05 \leq x \leq 0.3$) specimens slightly decreased with increasing Zr concentration. However, the sintered density was obtained over 93% relative density with Zr concentration from 0.05 to 0.3 mol.

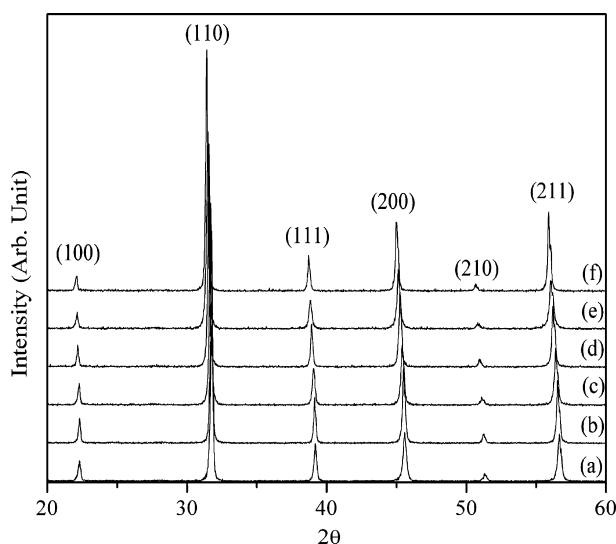


Fig. 1. XRD pattern for sintered specimen of $(\text{Ba}_{0.6}\text{Sr}_{0.4})(\text{Ti}_{1-x}\text{Zr}_x)\text{O}_3$ sintered at 1500 °C for 2 h: (a) 0.05 mol, (b) 0.1 mol, (c) 0.15 mol, (d) 0.2 mol, (e) 0.25 mol, (f) 0.3 mol.

Table 1

Lattice parameter of $(\text{Ba}_{0.6}\text{Sr}_{0.4})(\text{Ti}_{1-x}\text{Zr}_x)\text{O}_3$ ceramics sintered at 1500 °C for 2 h

Zr (mol)	0.05	0.1	0.15	0.2	0.25	0.3
a (Å)	3.9686	3.971	3.99	4.008	4.014	4.032

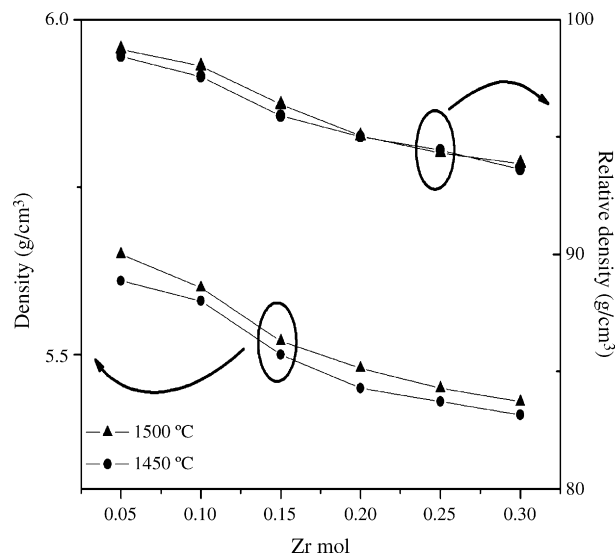


Fig. 2. Sintered densities of $(\text{Ba}_{0.6}\text{Sr}_{0.4})(\text{Ti}_{1-x}\text{Zr}_x)\text{O}_3$ ceramics with various sintered temperature for 2 h.

Fig. 3 shows microstructure of $(\text{Ba}_{0.6}\text{Sr}_{0.4})(\text{Ti}_{1-x}\text{Zr}_x)\text{O}_3$ ceramics sintered at 1450 °C for 2 h. The $(\text{Ba}_{0.6}\text{Sr}_{0.4})(\text{Ti}_{1-x}\text{Zr}_x)\text{O}_3$ ceramic was dense and homogeneously fine microstructure. The grain size decreased from over 20 to 2–3 μm with Zr concentration from 0.05 to 0.3 mol. The pore was observed and increased over the 0.15 mol of Zr concentration. Therefore, the bulk density was decreased due to the pore in the $(\text{Ba}_{0.6}\text{Sr}_{0.4})(\text{Ti}_{1-x}\text{Zr}_x)\text{O}_3$ ceramics.

Fig. 4 shows the temperature dependence of capacitance of $(\text{Ba}_{0.6}\text{Sr}_{0.4})(\text{Ti}_{1-x}\text{Zr}_x)\text{O}_3$ ceramics sintered at 1500 °C for 2 h as a function of x measured at 1 MHz. The Curie temperature shifted negative direction from 3.1 to –95 °C with increasing Zr concentration from 0.05 to 0.3 mol. At higher Zr concentrations ($0.2 < \text{Zr}$), phase transitions showing broad capacitance maxima are called diffuse phase transition.^{7,8} According to Tang et al.,⁹ in the solid solution of $(\text{Ba}_{0.6}\text{Sr}_{0.4})(\text{Ti}_{1-x}\text{Zr}_x)\text{O}_3$ Ba ions occupy the A sites of the ABO_3 perovskite structure. Zr and Ti ions occupy the B sites, and the ionic radius of Zr^{4+} (0.72 Å) is larger than that of Ti^{4+} (0.609 Å), therefore, at higher Zr contents, the $(\text{Ba}_{0.6}\text{Sr}_{0.4})(\text{Ti}_{1-x}\text{Zr}_x)\text{O}_3$ bulk ceramics show a broad capacitance–temperature curve at the vicinity of the transition temperature T_m , which is caused by an inhomogeneous distribution of Zr ions in the Ti sites and mechanical stress in the grain.

The P – E hysteresis loop of $(\text{Ba}_{0.6}\text{Sr}_{0.4})(\text{Ti}_{1-x}\text{Zr}_x)\text{O}_3$ ceramics measured at room temperature. The slim hysteresis loop with almost zero remnant polarization indicated that $(\text{Ba}_{0.6}\text{Sr}_{0.4})(\text{Ti}_{1-x}\text{Zr}_x)\text{O}_3$ ceramics existed in paraelectric phase at room temperature. It is known that the polarization described the following Eqs. (1) and (2).

$$P = \varepsilon_0 E(k - 1) \quad (1)$$

$$\frac{P}{E} = \varepsilon_0(k - 1) \quad (2)$$

With understanding of the dielectric constant verse electric field of $(\text{Ba}_{0.6}\text{Sr}_{0.4})(\text{Ti}_{1-x}\text{Zr}_x)\text{O}_3$ ceramics, it was calculated

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