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Improvement of dielectric loss of (Ba,Sr)(Ti,Zr)O_3 ferroelectrics for tunable devices

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Abstract

$(Ba_{0.6}Sr_{0.4})(Ti_{1-x}Zr_x)O_3$ $(0.05 \le x \le 0.3)$ 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 $(Ba_{0.6}Sr_{0.4})(Ti_{1-x}Zr_x)O_3$ 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 $(Ba_{0.6}Sr_{0.4})TiO_3$ ferroelectrics, which are limelight materials for tunable devices such as varactors, phase shifters and frequency agile filters, etc.

Keywords: Ferroelectrics; Dielectrics; Perovskites; Tunable devices

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, $Ba_{0.6}Sr_{0.4}TiO_3$ 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 $BaTiO_3$ can be systematically changed in $BaTiO_3$ by chemical substitution of barium and/or titanium by a wide variety of isovalent and aliovalent dopants.[2,4] Recently, $BaTiO_3$-$BaZrO_3$-$CaTiO_3$ has been shown as an alternative to BST in fabrication of ceramic capacitors because Zr^{4+} is chemically more stable than Ti^{4+}.[5,6] In this paper, we have studied the effect of Zr^{4+} ion for substitution for Ti^{4+}.

2. Experimental procedures

$(Ba_{0.6}Sr_{0.4})(Ti_{1-x}Zr_x)O_3$ $(0.05 \le x \le 0.3)$ were synthesized by the conventional solid-state reaction method and the starting materials were $SrCO_3$, TiO_2, ZrO_2 (Aldrich, 99.9%), $BaCO_3$ (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/cm^2 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

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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 Kα 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 $(Ba_{0.6}Sr_{0.4})(Ti_{1-x}Zr_x)O_3$ $(0.05 \le x \le 0.3)$ ceramics sintered at 1500 °C for 2 h. The sintered $(Ba_{0.6}Sr_{0.4})(Ti_{1-x}Zr_x)O_3$ ceramics were single phase of cubic (*Pm*3*m*) structure. The (1 0 0) peak was shifted low angle with increasing Zr concentration. That means increasing the lattice parameter of $(Ba_{0.6}Sr_{0.4})(Ti_{1-x}Zr_x)O_3$ 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 $(Ba_{0.6}Sr_{0.4})(Ti_{1-x}Zr_x)O_3$ 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/cm^3 with increasing Zr concentration from 0.05 to 0.3 mol. The relative density of $(Ba_{0.6}Sr_{0.4})(Ti_{1-x}Zr_x)O_3$ $(0.05 \le x \le 0.3)$ 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.

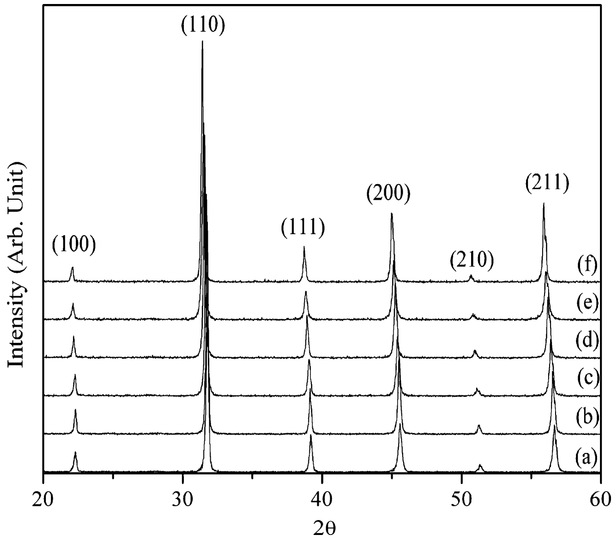

Fig. 1. XRD pattern for sintered specimen of $(Ba_{0.6}Sr_{0.4})(Ti_{1-x}Zr_x)O_3$ sintered at 1500 °C for 2 h: (a) 0.05 mol, (b) 0.1 mol, (c) 0.15 mol, (d) 0.2 mol, (e) 0.25 mol, (f) 0.3 mol.

Table 1
Lattice parameter of $(Ba_{0.6}Sr_{0.4})(Ti_{1-x}Zr_x)O_3$ 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

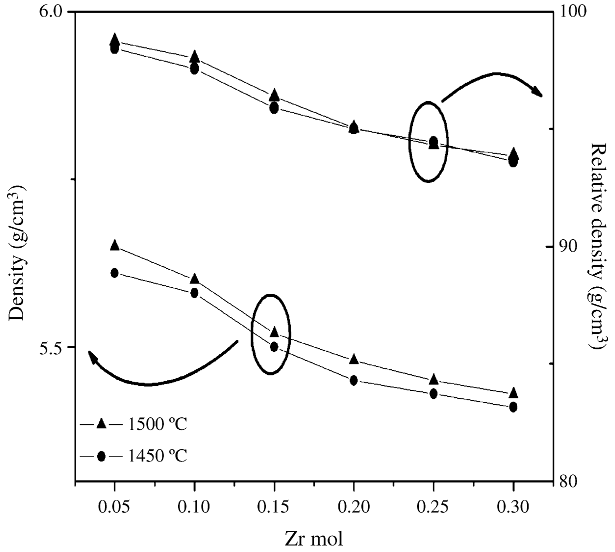

Fig. 2. Sintered densities of $(Ba_{0.6}Sr_{0.4})(Ti_{1-x}Zr_x)O_3$ ceramics with various sintered temperature for 2 h.

Fig. 3 shows microstructure of $(Ba_{0.6}Sr_{0.4})(Ti_{1-x}Zr_x)O_3$ ceramics sintered at 1450 °C for 2 h. The $(Ba_{0.6}Sr_{0.4})(Ti_{1-x}Zr_x)O_3$ 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 $(Ba_{0.6}Sr_{0.4})(Ti_{1-x}Zr_x)O_3$ ceramics.

Fig. 4 shows the temperature dependence of capacitance of $(Ba_{0.6}Sr_{0.4})(Ti_{1-x}Zr_x)O_3$ 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 < 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 $(Ba_{0.6}Sr_{0.4})(Ti_{1-x}Zr_x)O_3$ 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 $(Ba_{0.6}Sr_{0.4})(Ti_{1-x}Zr_x)O_3$ 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 $(Ba_{0.6}Sr_{0.4})(Ti_{1-x}Zr_x)O_3$ ceramics measured at room temperature. The slim hysteresis loop with almost zero remnant polarization indicated that $(Ba_{0.6}Sr_{0.4})(Ti_{1-x}Zr_x)O_3$ ceramics existed in paraelectric phase at room temperature. It is known that the polarization described the following Eqs. (1) and (2).

$$P = \varepsilon_0 E(k-1) \tag{1}$$

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

With understanding of the dielectric constant verse electric field of $(Ba_{0.6}Sr_{0.4})(Ti_{1-x}Zr_x)O_3$ ceramics, it was calculated

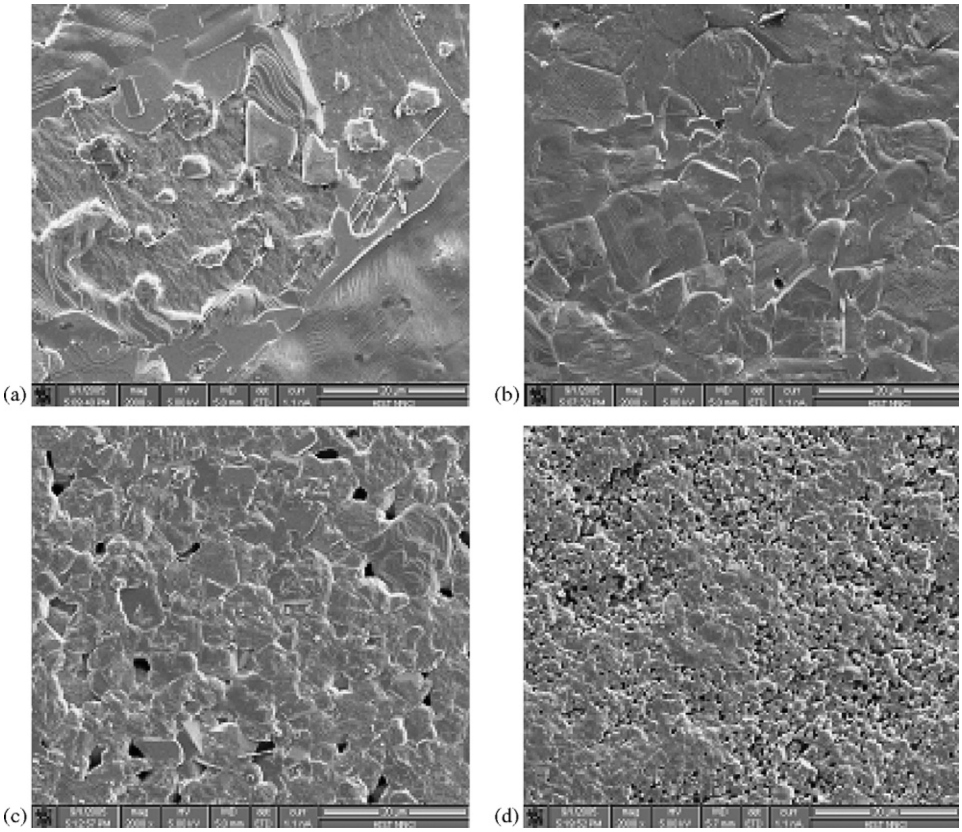

Fig. 3. SEM photographs of $(Ba_{0.6}Sr_{0.4})(Ti_{1-x}Zr_x)O_3$ ceramics sintered at 1450 °C for 3 h: (a) 0.05 mol, (b) 0.1 mol, (c) 0.2 mol, (d) 0.3 mol.

from Eq. (2). The tunability can be calculated by using the Eq. (3).

$$\text{Tunability }(\%) = \frac{\varepsilon_0 - \varepsilon_v}{\varepsilon_0} \times 100 \quad (3)$$

where ε_0 and ε_v represent the dielectric constant at zero and applied electric field, respectively. The dielectric constant verse electric field of $(Ba_{0.6}Sr_{0.4})(Ti_{1-x}Zr_x)O_3$ ceramics and tunability as a function of x measured at $E = 30$ kV/cm is depicted in Fig. 5. At room temperature, the tunability of $(Ba_{0.6}Sr_{0.4})(Ti_{1-x}Zr_x)O_3$ ceramics is decreased with increasing Zr content. The tunabilities measured at room temperature under the biasing field of $E = 30$ kV/cm for $(Ba_{0.6}Sr_{0.4})(Ti_{1-x}Zr_x)O_3$ ceramics are 65% ($x = 0.05$), 63% ($x = 0.1$), 48% ($x = 0.2$), and 35% ($x = 0.3$), respectively. The high tunability of the $(Ba_{0.6}Sr_{0.4})(Ti_{0.95}Zr_{0.05})O_3$ ceramics near the transition temperature is expected.[10] The decrease of tunability with the increase of Zr content meant the decreasing nonlinearity due to the lower proportion of ferroelectric range.[5]

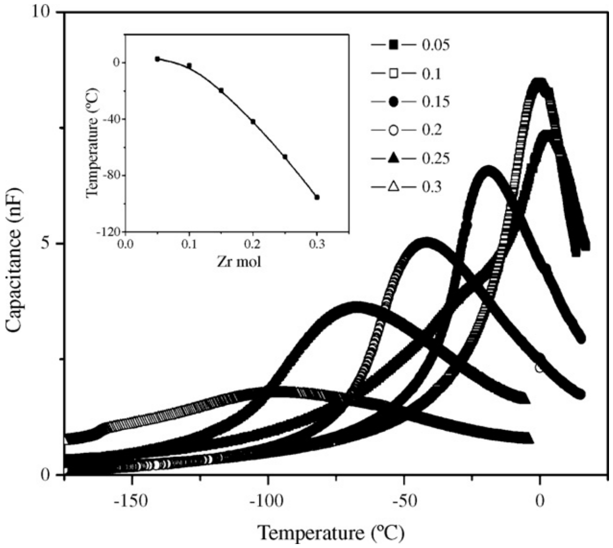

Fig. 4. The Curie temperature of sintered specimen of $(Ba_{0.6}Sr_{0.4})(Ti_{1-x}Zr_x)O_3$ with sintered at 1500 °C for 2 h at 1 MHz.

Fig. 6 shows dielectric constant and loss (tan δ) of $(Ba_{0.6}Sr_{0.4})(Ti_{1-x}Zr_x)O_3$ ceramics sintered at various temperature for 2 h as a function of x at 1 MHz. The dielectric constant of $(Ba_{0.6}Sr_{0.4})(Ti_{1-x}Zr_x)O_3$ ceramics decreased from 4985 to 1064 sintered at 1500 °C for 2 h. It is expected that the decrease of dielectric constant by substitution of Zr occurs because a slightly large Zr^{4+} ion (0.72 Å) is incorporated to a B-site Ti^{4+} with slightly smaller ionic radius (0.609 Å) hence, it is uneasily displaced under an electric field. This result is reasonable when we think over that an increase of Zr concentration slightly decreased the dielectric constant as reported by Kucheiko et al.[11,12] The dielectric loss decreased from 0.0022 to 0.0004 with increasing Zr concentration from 0.05 to 0.15 mol and then increased to 0.0275 with Zr concentration until 0.3 mol. The relationship between dielectric loss and substitution of Zr concentrations revealed the same trend with those between the

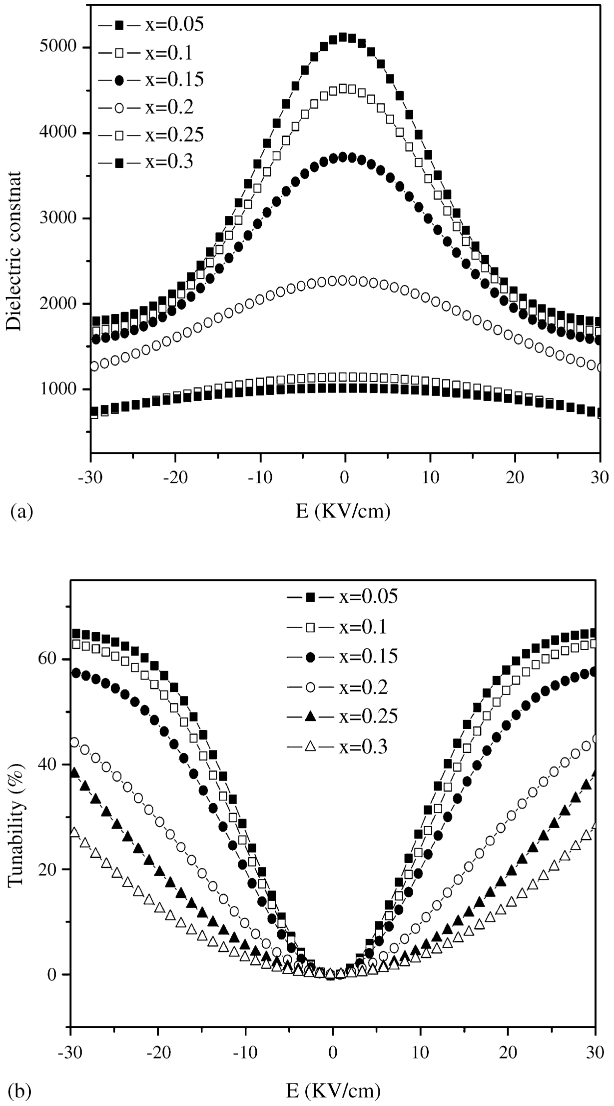

Fig. 5. (a) Dielectric constant vs. electric field, (b) tunability of $(Ba_{0.6}Sr_{0.4})(Ti_{1-x}Zr_x)O_3$ with sintered at 1500 °C for 2 h.

microstructure of $(Ba_{0.6}Sr_{0.4})(Ti_{1-x}Zr_x)O_3$ ceramics and them. It was worth nothing that Zr concentration reduced the dielectric loss of $(Ba_{0.6}Sr_{0.4})(Ti_{1-x}Zr_x)O_3$ ceramics which had good sinterability (over 95%).[12]

The figure of merit (FOM) is calculated by using the Eq. (4).

$$\mathrm{FOM} = \frac{\text{Tunability (\%)}}{\tan\delta} \tag{4}$$

The figure of merit value is shown in Fig. 7 measured at room temperature, under a bias field of 30 kV/cm. The figure of merit value increased until $x = 0.15$ because of the decrease of dielectric loss value dramatically, however, it was steeply decreased over 0.15 mol because of the increase of dielectric loss value and the decrease of tunability. The values of the figure of merit versus Zr concentration with a maximum value of FOM = 1260 and 1425 were found at $x = 0.1$ and 0.15. The result also implies that the optimum conditions of the ceramics for possible tuning applications at room temperature can be found at $x = 0.1$ and 0.15.

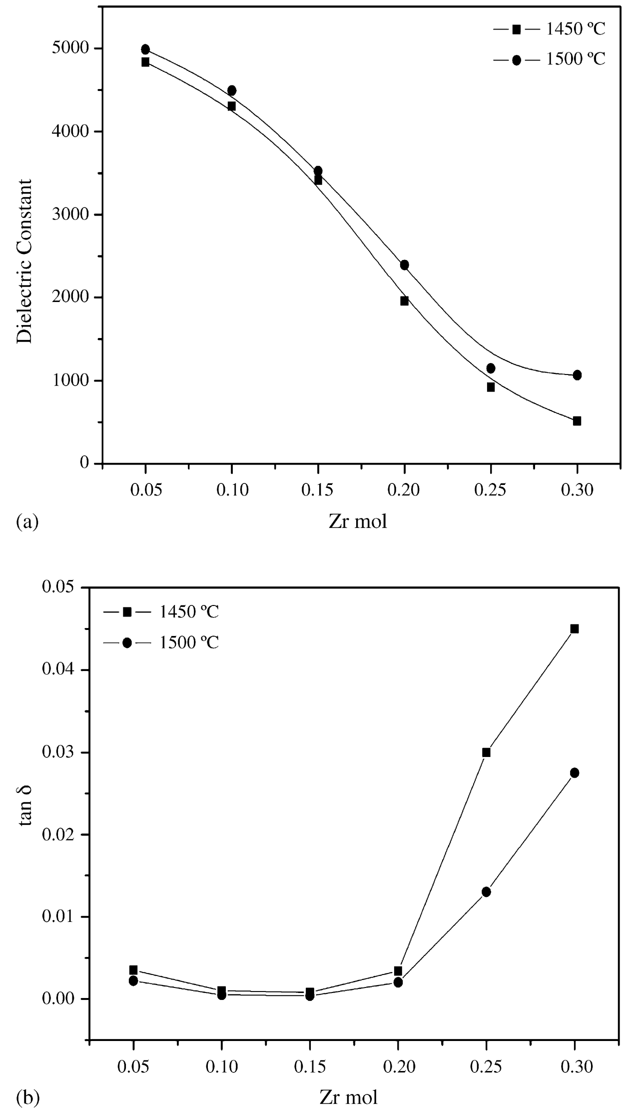

Fig. 6. (a) Dielectric constant, (b) dielectric loss of $(Ba_{0.6}Sr_{0.4})(Ti_{1-x}Zr_x)O_3$ ceramics with various sintered temperature for 2 h.

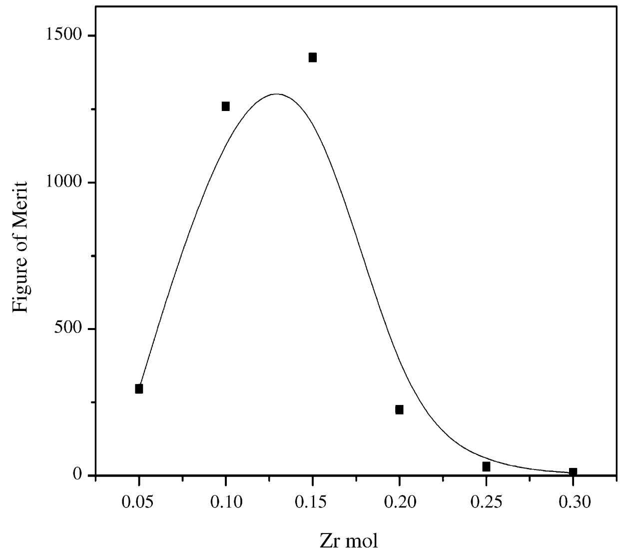

Fig. 7. Figure of merit of $(Ba_{0.6}Sr_{0.4})(Ti_{1-x}Zr_x)O_3$ ceramics sintered temperature at 1500 °C for 2 h.

4. Conclusions

$(Ba_{0.6}Sr_{0.4})(Ti_{1-x}Zr_x)O_3$ $(0.05 \leq x \leq 0.3)$ 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 $(Ba_{0.6}Sr_{0.4})(Ti_{1-x}Zr_x)O_3$ 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 $(Ba_{0.6}Sr_{0.4})TiO_3$ ferroelectrics, which are limelight materials for tunable devices such as varactors, phase shifters and frequency agile filters, etc.

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