

# Low-temperature dielectric and impedance properties of $Ba_{1-x}Sr_xTiO_3$ and $BaTi_{1-x}Ta_xO_3$ ceramics

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# Abstract

In this work, two series of BaTiO3-based ceramics,  $Ba_{1-x}Sr_xTiO_3$  (x = 0, 0.2, 0.4, 0.6, 0.8) and  $BaTi_{1-x}Ta_xO_3$  (x = 0.03, 0.06, 0.075, 0.09, 0.1), were synthesized by using standard solid-state reaction method at 1350 °C, and then sintered at 1400 °C for 10 h in air. Frequency-dependent dielectric and impedance properties were investigated at low temperature range of 100–300 K. The changes in dielectric properties of the  $Ba_{1-x}Sr_xTiO_3$  ceramics are believed to originate from the phase transition due to the different A-site  $Sr^{2+}$  doping concentration. The local electron-pinned defect-dipole effect is responsible for the enhancement of dielectric constant observed in the B-site  $Ta^{5+}$  doped  $BaTi_{1-x}Ta_xO_3$  ceramics. The complex impedance analysis was used to discern the temperature and frequency dependence of grains and grain boundaries responses. The results suggest that A- and B-site doped  $BaTiO_3$  ceramics can be applied for different dielectric devices at low temperatures.

Keywords: perovskites, doping, dielectric properties, impedance analysis

# I. Introduction

Traditional ABO<sub>3</sub> perovskite-type oxide materials have attracted extensive interest due to their ferroelectric, piezoelectric, pyroelectric and dielectric properties and potential applications such as storage devices, phase shifters, microelectromechanical systems, multilayer ceramic capacitors and optoelectronic devices [1– 5]. Specifically, the notable barium titanate (BaTiO<sub>3</sub>, BTO), strontium titanate (SrTiO<sub>3</sub>, STO) and their equivalent substitute materials are potential candidates for these applications.

It is well known that ion-doping is an effective way to improve the physical properties of oxide materials. For example, the leakage current density, ferroelectric polarization and dielectric loss of BiFeO<sub>3</sub> ceramics have been improved by  $Dy^{3+}$  doping [6]. (Bi<sub>0.5</sub>Na<sub>0.5</sub>)<sub>0.94</sub>Ba<sub>0.06</sub>TiO<sub>3</sub> ceramics modified with 0.3 wt.% Sm<sub>2</sub>O<sub>3</sub> exhibit excellent piezoelectric properties [7]. At room temperature, BTO crystallizes in a tetragonal structure, while STO in a cubic structure. By A-site substitution, Ba<sub>1-x</sub>Sr<sub>x</sub>TiO<sub>3</sub> (BST) ceramics exhibit attractive dielectric properties, high breakdown strength, and good thermal stability due to the

microstructure changes according to the different doping concentration x [8,9]. It is worth noting that BST is expected to replace silicon dioxide nowadays, which is a traditional dielectric material and can provide the required charge storage density [10]. Moreover, excellent ferroelectric and dielectric properties have been reported for BTO ceramics by B-site substitution with Zr<sup>4+</sup> ions (BZT) [11]. For BZT materials, doping with  $\mathrm{Zr}^{4+}$  ions can reduce the phase transition temperature, and the isovalent substitution can improve the ferroelectric and piezoelectric properties, which is related to the thermal promotion of domain switching. This creates a feasible example for the study of lead-free piezoelectric ceramics [12,13]. The radius of  $Ta^{5+}$  is 0.64 Å, which is smaller than the radius of  $Zr^{4+}$  (0.72 Å), and closer to the radius of  $Ti^{4+}$  (0.61 Å). This makes the studies on the dielectric and impedance properties of  $BaTi_{1,r}Ta_rO_3$ (BTT) well worth looking into.

In low-temperature applications, BST and BTT materials have shown great potential in a variety of fields, including superconducting and low-temperature electronics [14,15]. For instance, BST and BTT materials can be used to manufacture superconducting inductors, which are commonly employed in low-temperature magnet systems and superconducting quantum interference devices [16]. In addition, their high dielectric con-

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stants at low temperatures make them ideal for producing low-temperature capacitors, which are widely used in low-temperature electronic experiments and applications [17].

Considering the size of doping ions, the A- and Bsite substitution in  $ABO_3$  perovskite-type oxides is controlled by an allowable tolerance factor [18,19]:

$$\tau = \frac{r_A + r_O}{\sqrt{2}(r_B - r_O)} \tag{1}$$

where  $r_A$  and  $r_B$  represent the radii of the ions at position A and B, respectively,  $r_O$  is the radius of the ion at position O. If the factor  $\tau$  is within the range of 0.77– 1.10, the atoms on the A or B sites can be replaced by the dopant ions to form a continuous solid solution. The calculated values of  $\tau$  for BST and BTT are 1.00– 1.06 and 1.04–1.06, respectively, suggesting that these materials are available as substitution-doping oxides. In this paper, perovskite-type BST and BTT ceramics with various doping concentrations were fabricated by using solid-state reaction method. The effects of A- and Bsite doping on the dielectric and impedance properties of BTO-based ceramics were investigated at low temperatures.

# **II. Experimental details**

## 2.1. Processing of BST ceramics

 $Ba_{1-x}Sr_xTiO_3$  ceramics were synthesized by solidstate reaction using  $BaCO_3$ ,  $SrCO_3$  and  $TiO_2$  as raw materials with purity of 99.95% (Macklin Chemical Co. Ltd, Shanghai, China). Five samples were prepared by setting x = 0, 0.2, 0.4, 0.6 and 0.8, and the corresponding labels were denoted as BST00, BST02, BST04, BST06 and BST08, respectively. The stoichiometric amounts of the precursor powders were weighed by using electronic precision balance, fully mixed and milled to produce a uniform mixture and pre-sintered in an alumina crucible placed in a muffle furnace at 1350 °C for 4 h. The synthesized BST powders were placed in a cylindrical matrix and pressed uniaxially at a pressure of 200 MPa to obtain high-density pellets with a diameter of 10 mm and a thickness of 3 mm, which were sintered at 1400 °C for 10 h to fabricate BST ceramic samples. By using the Archimedes method, the bulk densities of the sintered samples were determined to be about 93–96 %TD.

## 2.2. Processing of BTT ceramics

BaTi<sub>1-x</sub>Ta<sub>x</sub>O<sub>3</sub> samples were prepared through conventional solid-state reaction process, using TiO<sub>2</sub> (99.9%), BaCO<sub>3</sub> (99.99%) and Ta<sub>2</sub>O<sub>5</sub> (99.8%) as raw materials purchased from Macklin Chemical Co. Ltd, Shanghai, China. Five samples were prepared by setting x = 0.03, 0.06, 0.075, 0.09 and 0.1, and the corresponding labels were denoted as BTT03, BTT06, BTT075, BTT09 and BTT10, respectively. The stoichiometric amounts of the raw materials were ground, mixed in an agate mortar and calcined at temperature of 1350 °C for 4 h. By dry pressing under a pressure of 180 MPa, a disk with a diameter of 10 mm and a thickness of about 3 mm was formed. After sintering at 1400 °C for 10h, BTT ceramic samples with bulk density greater than 95 % TD were obtained.

### 2.3. Characterization and measurements

Crystallization of the fabricated BST and BTT samples was analysed by X-ray diffraction (XRD) using a Rigaku (D/max-2400, Japan) diffractometer with Nifiltered Cu K $\alpha$  radiation. To characterize the microstructure, surface images of the prepared samples were taken with scanning electron microscope (SEM JEOL-JSM-7610F). For dielectric and impedance measurements, silver electrodes with a 0.2 mm diameter were sputtered on both sides of the samples by using a shadow mask. Low-temperature dependence of complex dielectric properties were measured on a QuadTech 1730 LCR Digibridge over a frequency range of 100 Hz–1 MHz. The impedance spectroscopy was examined by using a HP4194A analyser with signal amplitude of 50 mV. Data were taken in temperature range of 100–300 K.



Figure 1. XRD patterns of the synthesized BST ceramics (a) and the variation of *c/a* with the concentration *x* (b)

Table 1. Calculated a and a	values for the BST	ceramics samples
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	BST00	BST02	BST04	BST06	BST08
a [Å]	3.994	3.990	3.912	3.910	3.908
c [Å]	4.038	4.025	3.919	3.914	3.911

Table 2. Calculated a and c values for the BTT ceramics samples

	BST00	BST02	BST04	BST06	BST08
a [Å]	3.996	3.998	4.008	4.010	4.022
c [Å]	4.040	4.042	4.052	4.054	4.066



Figure 2. XRD patterns of the synthesized BTT ceramics (a) and shift of (101) peaks (b)

# III. Results and discussion

# 3.1. XRD analysis

Figure 1a shows XRD patterns of the fabricated BST ceramic samples with different *x* values. The XRD peaks of the samples BST00 and BST02 can be indexed to a tetragonal perovskite phase with space group *P4mm*, while the XRD peaks of the BST04, BST06 and BST08 ceramics are related to a cubic phase with space group  $Pm\bar{3}m$ . This structural change means that the prepared BST samples transform from the ferroelectric state to paraelectric state when  $x \ge 0.4$ . The corresponding peaks shift toward higher  $2\theta$  angles as the radius of  $Sr^{2+}$  (1.13 Å) is smaller than that of Ba<sup>2+</sup> ion (1.35 Å). The calculated values of lattice constants *a* and *c* are listed in Table 1. The variation of c/a with the Sr<sup>2+</sup> concentration *x* is plotted in Fig. 1b, which clearly demonstrates the phase transformation.

XRD patterns of the BTT samples are shown in Fig. 2a. All diffraction peaks can be indexed to a tetragonal phase and no impurity could be detected indicating that the B-site doping with 10 at.% Ta<sup>5+</sup> does not change the structure of BTO seriously. However, it is observed that the diffraction peaks shift to lower  $2\theta$  angles with the increase of Ta<sup>5+</sup> content (Fig. 2b). The increased interplanar spacings are the reason for the variation of diffraction peak positions. The calculated values of lattice constants *a* and *c* are listed in Table 2. Figure 3 shows the schematic illustration of B-site doping in BTT crystal structure. As it is known, the size of Ta<sup>5+</sup> is larger than

that of Ti<sup>4+</sup>. Doping with larger ions will lead to the increased lattice constant, which is responsible for the shift of diffraction peaks.



Figure 3. Schematic representation of BTT crystal structure

#### 3.2. SEM analyses

Figure 4 shows a typical SEM image of the fabricated BST02 sample. The grain size was about  $3-5 \,\mu\text{m}$ , in agreement with the results of other perovskite ceramics sintered at the same temperature [20,21]. Although it has been reported that the grain size rises with the increase of sintering temperature [22,23], no noticeable change of the microstructure or grain size can be detected in the BST and BTT samples sintered at the same temperature. This result is consistent with the literature data [24].



Figure 4. SEM images of Ba<sub>0.8</sub>Sr<sub>0.2</sub>TiO<sub>3</sub> ceramics at different magnifications

#### 3.3. Dielectric measurements

Figure 5 shows the dielectric properties of the BST ceramic samples measured at room temperature in the frequency range of 100 Hz-1 MHz. For all the samples, the values of dielectric constant and dielectric loss decrease with the increase of frequency, and reach a constant value when frequency is above 10 kHz. This is caused by the weak electron polarization at high frequencies [25,26]. For a lower  $\text{Sr}^{2+}$  doping, i.e. for the sample BST02, the increase of dielectric constant was observed, but with a further increase of doping concentration (the BST04, BST06, and BST08 ceramics) the dielectric constant decreases as a result of phase transformation (Fig. 5a). As shown in Fig. 5b, the dielectric loss of the BST samples increases with the increase of



Figure 5. Frequency-dependent dielectric constant and dielectric loss for the BST samples at room temperature

Sr content and it is between 0.00257–0.748. Defects and oxygen vacancies, which cannot be avoided and are very common in titanates, in the prepared samples play a role for this result [27]. Moreover, theoretical calculations predict a number of defect states within the BST band gap [28]. The formation of these defects is attributed to vacancies in the Ba and Sr as well as the O site of BST lattice. The band gap of BST increases with the increase in Sr<sup>2+</sup> doping level. More defect states can lead to the increased dielectric loss.

Generally, the exponential growth of dielectric loss indicates that the relaxation is related to the jump of carrier ions and the appropriate relaxation of surrounding ions. This behaviour can be described by the Universal Dielectric Response (UDR) model [29]:

$$f \cdot \varepsilon' = f \cdot \varepsilon_{\infty} + \frac{A}{\varepsilon_0} \tan\left(\frac{s\pi}{2}\right) f^s$$
 (2)

and

$$f \cdot \varepsilon'' = \frac{A}{\varepsilon_0} f^s \tag{3}$$

where  $\varepsilon_{\infty}$  is the high-frequency value of  $\varepsilon'(\omega)$ ,  $\varepsilon_0$  is the electric permittivity of free space, A and s are constants.

According to Eqs. 2 and 3, a straight line with a slope of s should be obtained in the plot of  $\log f \cdot \varepsilon' vs. \log f$ and  $\log f \cdot \varepsilon''$  vs.  $\log f$  at a given temperature. This relationship was confirmed by the log-log graphs for the BST04 sample shown in Fig. 6. By linear fitting, the plot of log  $f \cdot \varepsilon'$  vs. log f (Fig. 6a) gives  $s \sim 0.74$ , while that of log  $f \cdot \varepsilon''$  vs. log f (Fig. 6b) gives s = 0.26 - 0.28. The obtained values of s are consistent with the UDR assumption. The *s* value is a shape parameter that reflects the polarizability, complexity and frequency response characteristics of the dielectric material [29]. For BST and BTT perovskite oxide materials, the s value usually reflects the complexity of the internal structure and the influence of non-linear polarization behaviour. Specifically, the s value can be used to evaluate the polarization capability, frequency response characteristics and nonlinear polarization behaviour of the dielectric material. The obtained s value gives a better understanding of the dielectric properties of these materials, and a theoretical basis can be provided for their applications.



Figure 6. Logarithmic diagrams of frequency dependence of  $f \cdot \varepsilon'$  and  $f \cdot \varepsilon''$  for BST04 sample at given temperatures

Figure 7 shows the temperature-dependent dielectric constant of the prepared samples at f = 10 kHz in the low temperature range of 100–300 K. The peaks for the BST04, BST06 and BST08 samples indicate the Curie temperature of  $T_C = 265$ , 190 and 150 K, respectively. When the temperature is lower than  $T_C$ , the BST ceramics will spontaneously polarize, and the dipole will act to form the internal battery. However, when the temperature is higher than  $T_C$ , the BST ceramics acts in a paraelectric state and the dipole direction of the element



Figure 7. Temperature-dependent dielectric constant of BST samples at f = 10 kHz

is irregular, and the dielectric polarization and dielectric constant decrease with the increase of temperature [30]. As it is known, with the decrease in the doping concentration of  $\text{Sr}^{2+}$ ,  $T_C$  of the BST ceramics shifts to higher temperature. Thus, for the BST00 and BST02 samples, the Curie transition temperature is above 300 K. It has been reported that the variation of  $T_C$  of ABO<sub>3</sub> ceramics is related to the average ionic radius of the A-site cation [31]. The substitution of Ba<sup>2+</sup> ion (1.35 Å) with Sr<sup>2+</sup> ion (1.13 Å) will reduce the average ionic radius, thus stabilize the cubic phase, which leads to the decrease of  $T_C$  with the increased doping of Sr<sup>2+</sup>.

Figure 8 shows the dielectric constant and dielectric loss as a function of frequency for the BTT samples at room temperature. It can be seen that the dielectric properties are weakly dependent of the testing frequency except for the sample with higher Ta content. The dielectric constant of the BTT10 ceramics increases significantly with the decrease of frequency, and the dielectric loss peak appears around f = 7 kHz (Fig. 8). This can be attributed to the generation of electron traps, which can be expressed as:

$$2 \operatorname{Ta}_2 \operatorname{O}_5 \xrightarrow{\operatorname{BaTiO}_3} 4 \operatorname{Ta}_{\operatorname{Ti}}^{\bullet} + V_{\operatorname{Ti}}^{\bullet \bullet} + 10 \operatorname{O}_{\operatorname{O}}$$
(4)

When the doping concentration of  $Ta^{5+}$  increases, it is expected that  $Ta^{5+}$  ions will gather at the grain boundary because of the driving force of electrostatic force and elastic strain energy. Therefore, the positively charged grain-boundary cores will be produced due to the charged  $Ta_{Ti}^{\bullet}$  defects. The charged defects, giving rise to the large defect-dipole clusters, are responsible for the large dielectric constant of the BTT10 sample. When the  $Ta^{5+}$  doping concentration is lower than 10%, the charged defect-dipole effects have less influence on the dielectric constant, and the dielectric behaviours of the BTT03, BTT06, BTT075 and BTT09 ceramics show approximate independence on the testing frequency.

Moreover, at lower Ta<sup>5+</sup> doping levels, dielectric properties of the BTT samples exhibit good low-temperature stability and Fig. 9 shows the temperature



Figure 8. Frequency-dependent dielectric constant and loss (inset) for the BTT samples at room temperature



Figure 9. Temperature-dependent (a) dielectric constant and (b) loss of BTT samples at f = 10 kHz

dependence of dielectric constant and dielectric loss at f = 10 kHz. The corresponding values are almost independent of the temperatures in the range of 100–300 K. The changing rate of dielectric constant, defined by:

$$r_{\varepsilon} = \frac{\varepsilon_T - \varepsilon_{300\,\mathrm{K}}}{\varepsilon_{300\,\mathrm{K}}} \tag{5}$$

is below 19%, and that of dielectric loss, defined by:

$$r_{\tan\delta} = \frac{\tan \delta_T - \tan \delta_{300\,\mathrm{K}}}{\tan \delta_{300\,\mathrm{K}}} \cdot 100 \tag{6}$$

is below 5.5% for all the samples. The good temperature stability suggests the low temperature coefficient of dielectric properties, which may expand the application of Ta-doped BTO materials to low-temperature fields.

## 3.4. Impedance analysis

Impedance analysis is considered to be an effective tool to study the dielectric behaviour of ceramic materials at the microscopic level [32]. By plotting the relationship between Z' and Z'', several arcs will appear at different frequencies depending on the relaxation time, where Z' and Z'' are real and imaginary parts of complex impedance  $Z^*$ . As the relaxation time of grains is shorter than that of grain boundaries, the arc corresponding to the grain effect locates at the higher frequency, while that corresponding to the grain boundary effect locates at the lower frequency. Figure 10 shows typical Z' versus Z'' plots for the BST04 sample at different temperatures in a frequency range of 100 Hz–1 MHz. At 300 K, two arcs corresponding to grain and grain boundary effects appear. The radii of these arcs increase dramatically with the decrease of the temperature, indicating the increase of grain and grain boundary resistance at lower temperatures. The arcs at 260, 220 and 180 K are not completely presented in the impedance spectrum, which means that the impedance responses of grain and grain boundary fall out of the scope of measuring frequencies.

The complex impedance spectra of the BTT samples at room temperature are shown in Fig. 11. The plot of the BTT10 ceramics displays two arcs, corresponding to the responses of grains and grain boundaries. With the decrease of  $Ta^{5+}$  doping concentration, the resistance of grains and grain boundaries increases, resulting in the enlarged arcs in the impedance plane. As it is known, the stoichiometric BTO is an insulator with large resistance. However, defects and electron donors will be inevitably produced during the substitution of  $Ti^{4+}$  with  $Ta^{5+}$  ions. The existing carriers at high doping concentrations will



Figure 10. Typical Z' versus Z" plots for BST04 sample at different temperatures



Figure 11. Z' versus Z" plots for the BTT samples at room temperature



Figure 12. Frequency-dependent Z" of BTT10 at different temperatures (a) and Arrhenius plots (b) for the BTT10 sample

result in the reduction of grains and grain boundaries resistance, which is responsible for the observed two arcs for the BTT10 sample.

To further analyse the impedance properties of the BTT10 sample, the frequency-dependent Z'' at different temperatures is shown in Fig. 12a. It can be seen that the value of Z'' decreases with the increase of temperature. This phenomenon can be explained by the fact that the energy of the polaron in ceramic materials increases with the increase of temperature, which makes it easier to carry out long-range or short-range hopping, leading to the reduction of Z''.

Moreover, the relaxation peaks, which move to higher frequencies with the increase of temperature, appear in the curves indicating that the relaxation process is a thermally activated mechanism. Generally, the relationship between the relaxation frequency f and corresponding temperature T conforms to the Arrhenius formula [33,34]:

$$f = f_0 \exp\left(-\frac{E_a}{K_B \cdot T}\right) \tag{7}$$

where  $f_0$  is the pre-exponential factor, K)B is the Boltzmann constant and  $E_a$  is the activation energy. Relaxation peak position versus 1/T is shown in Fig. 12b. The activation energy for the BTT10 sample, obtained by linear fitting, is 1.14 eV. The relaxation activation energy is mainly the free energy of carriers jumping between adjacent lattices. According to the previous studies, the relaxation energy caused by  $V^{\bullet \bullet}$  oxygen vacancy double ionization is between 0.6 and 1.2 eV, while the relaxation energy caused by single ionized oxygen vacancy  $V^{\bullet}$  is less than 0.6 eV in perovskite ceramics [35– 37]. When the relaxation activation energy is greater than 1.2 eV, it is mainly due to the cation defects. It can be seen that the relaxation process of BTT10 ceramic sample is related to the double ionization of oxygen vacancy.

## **IV. Conclusions**

Perovskite-type oxide materials  $Ba_{1-x}Sr_xTiO_3$  (x = 0, 0.2, 0.4, 0.6 and 0.8) and  $BaTi_{1-x}Ta_xO_3$  (x = 0.03, 0.06, 0.075, 0.09 and 0.1) were synthesized by using standard solid-state reaction method at 1350 °C and finally sintered at 1400 °C. Effects of A- and B-site doping on the low-temperature dielectric and impedance properties of BaTiO<sub>3</sub>-based ceramics were studied. The phase transition in  $Ba_{1-r}Sr_rTiO_3$  due to the change in Sr<sup>2+</sup> doping concentration was observed, i.e. the samples with low Sr<sup>2+</sup> content have tetragonal perovskite phase, while if the concentration of  $Sr^{2+}$  is  $\ge 4$  at.% the samples have cubic symmetry. For  $BaTi_{1-x}Ta_xO_3$  ceramics, B-site Ta5+ doping up to 10 at.% does not change the crystal structure seriously. As the electronegativity of Ti<sup>4+</sup> and Ta<sup>5+</sup> is different, the local electron-pinned defect-dipole effect is responsible for the increase of dielectric properties with the increase of Ta<sup>5+</sup> doping concentration. The impedance properties of the prepared samples were studied at low temperatures.

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