Effects of Oxygen Vacancies on Dielectric Properties and Relaxor Behavior of Ba(Zr$_x$Ti$_{1-x}$)O$_3$ Ceramics

Xiang Li$^{1,2}$, Zheng Sun$^{1,*}$, Yuan Zhang$^3$, Dianchen Huang$^1$ and Jitao Hu$^1$

1 School of Integrated Circuit Science and Engineering, Tianjin University of Technology, Tianjin, China.
2 Tianjin Key Laboratory of Thin Film Electronics and Communication Devices, Tianjin University of Technology, Tianjin, China.
3 School of Electronic Engineering, Tianjin University of Technology and Education, Tianjin, China.
Email: sz_tjut@163.com

Abstract. By comparing the structure, dielectric and electrical conduction properties of sintered Ba(Zr$_{0.15}$Ti$_{0.85}$)O$_3$ ceramics (short as BZT15) annealed in air and oxygen atmosphere was conducted to explore the impact of oxygen vacancies (OVs) on them. The dielectric properties of the samples were studied as changing with temperature (260–400K) in the scope of frequency from 100 Hz to 100 kHz. A typical relaxor behavior was observed in BZT15 and the relaxor behavior was enhanced after oxygen annealing treatment, which confirmed that the relaxation process was connected with the OVs inside ceramics. The value of activation energy was calculated to be 1.76 eV, 1.79eV, and 1.85 eV for as-prepared, air and oxygen annealed samples, respectively. Besides, the dielectric relaxor behavior was found to be associated with the conductivity originated from the dipolar conduction and long-distance movement of doubly ionized OVs. More interestingly, compared with other ferroelectric materials, the higher activation energy of BZT15 ceramics revealed a weaker concentration of OVs for such dielectric materials.

Keywords. Ceramics, dielectric relaxation, oxygen vacancies.

1. Introduction
Perovskite oxides have attracted intensive attraction due to their potential application in many fields. Lead-based perovskite materials have drawn attention based on their outstanding dielectric, piezoelectric, and ferroelectric performance [1]. However the intrinsic volatilization and toxicity of lead based materials restricted the usage of these materials in environmentally friendly application. Hence attention was focused to develop lead-free perovskite materials.

Recently BaTiO$_3$-based materials were found to exhibit comparable properties to lead based PZT materials [2]. BaTiO$_3$-based materials have been applied in Multilayer ceramic capacitors (MLCCs) and piezoelectric actuators due to the large dielectric constant and high piezoelectric activity [3, 4]. Besides, BaTiO$_3$-based materials were found to be used in tunable microwave devices due to the higher tunability and good temperature stability [5].

Ba(Zr$_x$Ti$_{1-x}$)O$_3$ (short as BZT) is formed by Zr$^{4+}$ substituted for Ti$^{4+}$. It exhibits better temperature stability than Ba$_4$Sr$_3$TiO$_7$ in paraelectric phase due to the chemical stability of Zr$^{4+}$ [6]. It is found that a typical relaxation behavior appears for x ranged from 0.25 to 0.75 [7]. It has been recognized that the
relaxor behavior is ascribed to the formation of dynamic polar nano-regions (PNRs) [7]. However, the investigation of relaxor behavior for the content of zirconium near x=-0.2 remains limited.

Oxygen vacancies (OVs) were the main intrinsic defects in perovskite oxides which were proved to affect electrical performance [8]. Especially, OVs related dielectric relaxation behavior was existed in high temperature and low-frequency field. In this work, relaxor behavior was observed in BZT15, and analysis was performed to confirm whether the relaxor behavior was caused by OVs.

2. Experimental Procedures

BZT15 ceramics were prepared by solid-state reaction method. Based on the chemical composition, the powder raw materials of BaCO3 (99%), TiO2 (99%) and ZrO2 (99%) (supported by Sinopharm Chemical Reagent Co., Ltd, Shanghai, China) were weighted and uniformly ball milled in DI water for 6 h. After drying and calcination, the powders were granulated completely with 5wt% polyvinyl alcohol (PVA) and regrinding for 12h. Press the obtained powder material into pellets with thickness of 1mm and diameter of 10 mm. Then these disks were sintered at 1375°C for 4 h in air. The crystal structures of the sintered samples were determined via Powder X-ray diffractometer (D8-Focus; Bruker AXS GmbH, Karlsruhe, German). Observed the microstructure of the obtained samples by using field emission scanning electron microscopy (FE-SEM, S-4800, Hitachi, Ltd. Japan). In the temperature range of 260 to 400K, the temperature dependence of dielectric permittivity was measured with LCR meter (TH2828; Tonghui, Changzhou, Jiangsu, China) and a temperature chamber at different frequencies (from 100 Hz to 100 kHz).

3. Results and Discussion

Figure 1 shows the XRD patterns of BZT15 samples. All samples show a polycrystalline structure of pure cubic perovskite phase. The inset of figure 1 exhibits the surface topography of BZT15 ceramics observed by SEM. The grain structure was obvious, and the average grain size was 30~50 μm.

Figure 2 exhibits the change in dielectric constant and tangent loss of BZT15 with temperature at different frequencies. As seen in figure 2, typical frequency dispersion behavior was appeared, namely, the dielectric constant (\(\varepsilon'\)) decreases with the increase of frequency and \(T_m\) corresponded to the maximum value of \(\varepsilon'\) gradually shifts toward to high temperature. Besides, the dielectric loss increases with increasing measurement frequency.

Several polarization mechanisms were supposed to be related to the dielectric relaxor behavior. It is known that the low frequency region was related to space-charge polarization, interfacial polarization, and long-range structure disorder [9]. Thus, it is reasonable to deduce that the relaxation behavior may be attributed to oxygen vacancies (OVs).

![Figure 1](image1.png)

**Figure 1.** The XRD of the as-prepared BZT15 pellet. The inset shows the SEM image for the as-prepared pellet.

![Figure 2](image2.png)

**Figure 2.** Temperature dependences of dielectric constant and loss of BZT15 samples measured from 100Hz to 100 kHz.
OVs in perovskite oxides were often unavoidable and the high temperature caused relaxor behavior was reported to be related to this defect [10]. In order to identify whether the relaxor behavior was related to oxygen-vacancy, the annealing treatments in reducing and oxidizing ambient was often used [11]. Therefore, the dielectric properties of as-prepared and annealed treated BZT15 samples in this work were implemented. Figure 3(a) and (b) exhibit the temperature dependent permittivity (ε') of as-prepared, air and oxygen annealing treated (800°C, 2h) BZT15 samples measured at 100Hz and 1kHz, respectively. Obviously, dielectric relaxation behavior could be suppressed through annealing treatment.

Figure 4 depict the dielectric loss (tanδ) vs temperature of as-prepared, air and oxygen annealing treatments (800°C, 2h) BZT15 samples at the frequency of 100Hz and 1 kHz, respectively. As seen in figure 4 (a), the peak height of dielectric loss decreased from 0.0271 to 0.0191 for as-prepared and oxygen annealing treatment samples, respectively. Similar results were found in figure 4 (b). Besides, the corresponding temperature of loss peak of annealed BZT15 ceramics moves to higher temperature, which is a typical dielectric relaxation behavior.

Figure 3. Temperature dependences of ε' for as-prepared, air and oxygen annealed BZT15 samples, measured at frequencies (a) 100Hz and (b) 1kHz.

Figure 4. Temperature dependences of dielectric loss at the frequency of (a) 100Hz (b) 1kHz for BZT15 ceramics with different annealing treatments.
The peak height is proportional to the density of the relaxation units (oxygen vacancies), which can be explained by the point defect relaxation theory [12]. The activation energy ($E_a$) and relaxation time ($\tau$) follow the famous Arrhenius law:

$$\omega_0 = \omega_0 \exp\left(-\frac{E_a}{k_B T_m}\right)$$  \hspace{1cm} (1)

where $T_m$ is the absolute temperature, $\omega_0$ is characteristic frequency, $E_a$ is the activation energy and $k_B$ represents the Boltzmann constant.

The fitted results were shown in figure 5.

Figure 5. Plots of $\ln(\omega_p)$ versus $1000/T_m$ for BZT15 ceramics with various annealing treatments.

The fitted results ($E_a$) are 1.76 eV, 1.79 eV and 1.85 eV for as-prepared, air and oxygen annealed treatments BZT15 samples, respectively. Similar results had been reported in SrTiO$_3$ [11], Ba doped PZT [13] and (PbLa)(Zr$_{0.9}$Ti$_{0.1}$)O$_3$ [14].

It should be noted that $E_a$ slightly increases after air and O$_2$ annealed treatments. According to reports, this change is caused by the formation of “clusters” of OVs [15]. Compared with the individual OVs, the movement of this cluster requires lower energy. With increasing OVs concentration, the OVs clusters is formed which also strengthens the correlation of OVs and facilitates the movement of OVs, leading to the decrease of $E_a$ [16]. In this work, the concentration of OVs is suppressed by oxygenation treatment, which results in the increase of $E_a$. It is known that OVs related dielectric relaxation may be quantitatively similar for all perovskite oxides [9]. The higher $E_a$ in BZT15 ceramics may be caused by lower density of OVs [13].

It is accepted that grain boundary prevents OVs movement [17]. And OVs are not fixed in one unit cell, they migrate in the whole sample and lead to the appearance of ionic conductivity [18]. Temperature is the main factor to activate the OVs related dielectric relaxation [11]. It is naturally accepted that higher temperature may thermally “ionized” the OVs and promote the mobility of oxygen ions. Therefore, it is reasonably supposed that movement of relaxation peaks at high temperature may be related to the movement of OVs in BZT15 ceramics.

The ac conductivity can be concluded using the following formula:

$$\sigma^* = \sigma'' - i \omega \varepsilon_0 \varepsilon''$$  \hspace{1cm} (2)

where $\varepsilon^*$, $\omega$ represent the complex conductivity, the angular frequency and $\varepsilon'$, $\varepsilon''$ stand for the real and imaginary parts of the permittivity respectively. The ac conductivity can be concluded using the following formula:

$$\sigma' = \omega \varepsilon_0 \varepsilon''$$  \hspace{1cm} (3)
And based on Arrhenius equation:

$$\sigma' = \sigma_0 \exp\left(-\frac{E_{\text{cond}}}{k_B T}\right)$$

in which $\sigma_0$ and $E_{\text{cond}}$ are the invariable and activation energy for conduction, respectively. Figure 6 shows the Arrhenius plots at the frequency of 100Hz. As is known to all that the value of $E_a$ is supposed to be higher than $E_{\text{cond}}$ in dipolar conduction dominant relaxation mechanism. If not, $E_a$ would be close or less than $E_{\text{cond}}$ [19]. Compared $E_a$ (1.76eV, 1.79eV, 1.85eV) and $E_{\text{cond}}$ (1.13 eV, 1.49 eV, 1.84 eV), it can be seen that the relaxation process in BZT15 ceramics is governed by dipolar conduction process.

![Figure 6](image_url)

**Figure 6.** ln($\sigma'$) versus 1000/$T_m$ curves for BZT15 ceramics with various annealing treatments at 100Hz.

It is well known $E_a$ of the singly ionized OVs are around 0.7–0.8 eV and the values of $E_{\text{cond}}$ (1.13-1.84 eV) were very close to $E_a$ of doubly ionized OVs [20]. Therefore, it can be reasonably deduced that doubly ionized OVs are the mainly dominated relaxation mechanism in BZT15 ceramics.

4. Conclusions

BZT15 ceramics were fabricated by solid state route in this work. The changes in the dielectric properties of BZT15 with frequency and temperature were investigated. The values of $E_a$ and $E_{\text{cond}}$ increased after oxygen annealed treatments which confirmed that dielectric relaxor behavior in BZT15 ceramics was dominated by oxygen vacancies which can be prohibited through annealing treatments in air and O$_2$ atmosphere. Finally, the analysis results showed that movements of doubly-ionized OVs is the main mechanism in BZT15 samples.

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