High-temperature colossal dielectric behavior of BaZrO₃ ceramics

Lei Tong, Haibo Li, Wei Ni, Youmin Guo,* Qiuju Li, Hong Wang and Chunchang Wang*

BaZrO₃ (BZO) powders were synthesized by solution combustion based on the glycine nitrate process. The sintering conditions of the BZO sample were optimized by varying the sintering temperature and dwell time. The dielectric properties of the sintered samples were investigated in the temperature range of 300–1080 K and frequency range of 10² to 10⁶ Hz. The sample sintered at 1973 K for 12 h was found to show the best dielectric properties. Detailed investigations on this sample reveal an incipient ferroelectric behavior in the temperature range below 420 K and a colossal dielectric behavior above 420 K. The colossal dielectric behavior is composed of two thermally activated relaxations. The low-temperature relaxation was argued to be a dipolar relaxation caused by an oxygen vacancy hopping motion inside grains and the high-temperature one was ascribed to a Maxwell–Wagner relaxation due to the oxygen vacancies being blocked by the sample/electrode contacts.

1. Introduction

Materials showing colossal dielectric constants (CDCs, dielectric constants larger than 10⁶) have drawn considerable attention due to their promising potential for application in the area of device miniaturization and energy storage.¹⁻³ There are currently two main types of CDC material systems. The traditional type of CDC material is ferroelectric perovskites, which show dielectric constants up to 10⁴ to 10⁵ around the ferroelectric phase transition,⁴ but suffer from strong temperature dependence. Another type of CDC material system is the plethora of non-ferroelectric oxides represented by CaCu₃Ti₄O₁₂.⁵⁻⁷ The CDC behavior of this type of material is characterized by a colossal and temperature stable dielectric constant plateau around room temperature. This dielectric plateau decreases in a step-like manner to a low dielectric constant below 100, 120, and 200 K for Ba₂CoNbO₆,⁸ Na₀.₅Bi₀.₅Cu₃Ti₄O₁₂,⁹ and TbFeO₃ (ref. 10) recorded at 10 kHz, respectively. In order to circumvent this limitation, the search for materials exhibiting such kind of dielectric plateau at or above RM is of vital importance. Recently, our group has reported that CaLaAlO₄ ceramics showed CDC behavior in the temperature above RM.¹¹ The typical feature of this material is that it contains no transition metal ions and the CDC behavior is caused by the electromigration of oxygen vacancies. This work provides a heuristic hint to search for high-temperature CDC materials in oxides free of transition metal ions.

Proton conductors based on cerate and zirconate perovskite oxides have attracted considerable attention in recent years for electrochemical applications, such as fuel cells, separation membranes, and steam electrolyzers.¹²⁻¹³ Of the known perovskite-type proton conductors, there has been considerable experimental interest in acceptor-doped BaZrO₃ (BZO) due to its high proton conductivity in a cubic structure coupled with good chemical and mechanical stability.¹⁴⁻¹⁵ The electric properties of pure BZO, however, is dominated by oxygen vacancies.¹⁶⁻¹⁷ On the other hand, the Zr⁴⁺ is very stable (with respect to Ti⁴⁺). This fact makes BZO similar to a material free of transition metal ions. Therefore, high-temperature CDC behavior could be expected in BZO. However, to the best of our knowledge, dielectric properties of BZO were performed in low-temperature range below RM¹⁸ or on Ti-doped samples.¹⁹⁻²¹ There are no reports on the dielectric properties of BZO above RM.

In this paper, we performed investigations on high-temperature (300 to 1080 K) dielectric properties of BZO ceramics. As expected, the sample showed high-temperature CDC behavior composed of two relaxations. The mechanisms of these relaxations were discussed.
2. Experimental details

BZO samples were synthesized by solution combustion based on the glycine nitrate process. Stoichiometric amounts of barium nitrate [Ba(NO₃)₂] (0.04 mol) and zirconium nitrate (Zr(NO₃)₄·5H₂O) (0.04 mol) were dissolved in deionized water (800 mL) to form a solution. Glycine was then added at a molar ratio of glycine (0.16 mol) to total metallic cations of 2. The water in the solution was evaporated by heating over a hot plate while stirring until a gel was formed. The gel was moved to an electric oven at 513 K triggering auto-combustion. The resulting primary powders were further calcined at 1373 K for 5 h in ambient air. After cooling to room temperature naturally, pellets of 11 mm diameter and approximately 1 mm thickness were pressed and sintering at different conditions. The phase purity of the synthesized powders was characterized by X-ray diffraction (XRD) on a Rigaku SmartLab diffractometer (Rigaku Beijing Co., Beijing, China) with Cu Kα radiation. The microstructure and grain size of the sintered pellets were studied using a field-emission scanning electric microscope (SEM, Model S-4800, Hitachi Co., Tokyo, Japan). The temperature-dependent dielectric properties were measured using a Wayne Kerr 6500B precise impedance analyzer with the sample mounted in a holder placed inside a PST-2000HL dielectric measuring system (Partulab Co., Wuhan, China). The temperature variations were automatically controlled using a PCT10 Stanford temperature controller with a heating rate of 3 K min⁻¹. The ac measuring signal was 100 mV. Annealing treatments were performed in oxygen and nitrogen (both with purity > 99.999%) at 1073 K for 2 h with flow rate of 200 mL min⁻¹.

3. Results and discussion

Fig. 1 shows the room-temperature XRD pattern of synthesized BZO powders in the 2θ range of 20 to 80°. The pattern can be indexed based on a cubic structure with Pm₃m space group (JCPDS file no. 06-0399), and no impurity phases were observed. In order to obtain a BZO sample with high relative density for dielectric measurements, the pressed BZO pellets were sintered at different conditions.

Fig. 2 presents the SEM images of the sintered BZO ceramics. It can be seen that all samples present distinct grain structure. The average grain size and relative density are summarized in Table 1. From which, it is clearly seen that both the grain size and relative density increase with increasing sintering temperature and dwell time. The sample sintered at 1973 K for 12 h was found to show the highest relative density with a value of 98.1%.

Table 1 The average grain size, standard deviation and relative density of the BZO pellets prepared at different sintering conditions

<table>
<thead>
<tr>
<th>Sintering condition</th>
<th>Average grain size (μm)</th>
<th>Standard deviation (μm)</th>
<th>Relative density (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1773 K–12 h</td>
<td>1.05</td>
<td>0.20</td>
<td>90.8</td>
</tr>
<tr>
<td>1873 K–12 h</td>
<td>1.65</td>
<td>0.36</td>
<td>93.0</td>
</tr>
<tr>
<td>1923 K–6 h</td>
<td>2.73</td>
<td>0.62</td>
<td>95.2</td>
</tr>
<tr>
<td>1923 K–12 h</td>
<td>3.13</td>
<td>0.83</td>
<td>96.3</td>
</tr>
<tr>
<td>1973 K–6 h</td>
<td>3.47</td>
<td>0.92</td>
<td>96.3</td>
</tr>
<tr>
<td>1973 K–12 h</td>
<td>4.19</td>
<td>0.95</td>
<td>98.1</td>
</tr>
</tbody>
</table>
temperature plateau shows values larger than \(10^3\), indicating that the CDC behavior appears in these samples. To judge the merit of the CDC behavior, quality criteria, such as high dielectric constant, low dielectric loss, and good temperature stability have been put forward. Based on these factors, it is not difficult to find out that the sample sintered at 1973 K for 12 h shows the optimum properties. We, therefore, perform detailed dielectric investigations focusing on this sample in the following part.

Fig. 4 displays the temperature dependence of \(\varepsilon'(T)\) and \(\tan \delta(T)\) measured with various frequencies for BZO sintered at 1973 K for 12 h. In the temperature range below 420 K, both \(\varepsilon'(T)\) and \(\tan \delta(T)\) behave as plateaus independent of frequency and temperature. This can be ascribed to the intrinsic dielectric properties resulting from the electronic and/or ionic polarization. The flat dielectric constant was found to be \(\approx 34.8\), which agreed well with the previously reported values of 32–37. However, a careful examination reveals that the dielectric constant plateau is actually a frequency-independent decline similar to that found in SrTiO\(_3\) and KTaO\(_3\). This behavior is the typical feature for incipient ferroelectrics. To further confirm the incipient ferroelectric nature in the present sample, the data recorded with 1 MHz were fitted using the Barrett equation:

\[
\varepsilon'(T) = C \left( \frac{T_1}{T} \coth \left( \frac{T_1}{2T} \right) - T_0 \right)^{-1} + B
\]

where \(C\) is a constant, \(T_0\) is hypothetical Curie temperature, \(T_1\) is onset temperature of quantum fluctuations, and \(B\) is dielectric constant at high-frequency limit. The fitting result as well as the experimental data were given in the insert of Fig. 4(a). Perfect agreement between the experimental data and fitting result was achieved. The fitting yields the parameters of \(B = 28.54, C = 5454, T_1 = 309\) K, and \(T_0 = -18\) K. These values are comparable with those previously reported in BaZrO\(_3\), indicating that the incipient ferroelectric behavior exists in the present sample. With further increasing temperature, the sample exhibits CDC behavior similar to that reported in CaCu\(_3\)Ti\(_4\)O\(_{12}\). The CDC behavior is found to be composed of two stepwise increases occurring around 500 and 900 K (for the curve recorded under 100 Hz). Meanwhile, two sets of peaks in the curves of the dielectric loss tangent are observed. The positions of both sets of peaks shift to high temperature with increasing frequency. This indicates that there are two thermally activated relaxations in BZO. To discuss each relaxation clearly, the two relaxations were referred to as \(R1\) and \(R2\) in the order of ascending temperature.

To understand the mechanism of the observed relations, we try to calculate the relaxation parameters for each relaxation. But \(R2\) in \(\tan \delta(T)\) is obscured by the increasing background, which makes it difficult to deduce its position accurately. To overcome this shortcoming, the dielectric function of electric modulus \(M^* = M' + iM'' = 1/\varepsilon^*, \) where, \(j = \sqrt{-1}\) is applied. It was suggested that electric modulus could provide valuable information about relaxation mechanism in the absence of a well-defined dielectric loss peak in \(\tan \delta(T)\). Fig. 5 shows the imaginary part of the electric modulus \(M''(T)\) as a function of temperature under various frequencies ranging from 100 Hz to 1 MHz for BZO ceramics. Owing to the absence of the increasing background, a set of thermally activated relaxation can be clearly seen. The inset (a) is an enlarged view of the \(M''(T)\) curves in the high-temperature range as indicated by the rectangle. It clearly shows the high-temperature relaxation. The electric modulus spectra substantially confirm the two sets of relaxations in BZO. To calculate the relaxation parameters, the measuring frequency \((f)\) and the peak position \((T_p)\) was plotted according to the Arrhenius law:

\[
f = f_0 \exp(-E_a/k_B T_p)
\]

where \(f_0\) is eigenfrequency, \(E_a\) is activation energy for relaxation and \(k_B\) is Boltzmann constant. Arrhenius plots for \(R1\) and \(R2\) (closed points) along with the linear fits (straight lines through
Annealing case | Relaxation parameter | Relaxation parameter
---|---|---
As-prepared | $E_a$ (eV) | $f_0$ (Hz) | $E_a$ (eV) | $f_0$ (Hz)
O$_2$-annealed | 0.80 | $9.97 \times 10^{10}$ | 1.52 | $1.28 \times 10^{11}$
N$_2$-annealed | 0.94 | $1.2 \times 10^{12}$ | 1.83 | $6.31 \times 10^{13}$

In order to evidence this point, we conduct impedance analysis, as it is a powerful technique to separate the dielectric contributions from bulk (grain), grain boundary and contact effects. Fig. 6(a) and (b) displays the Nyquist plots ($Z''$ vs. $Z'$, where $Z'$ and $Z''$ are the real and imaginary parts of the complex impedance $Z^*$) of BZO sample measured at the temperatures of 450 and 730 K under different DC biases. The complex impedance spectra at 450 K behave as a semicircular arc independent of DC bias confirming bulk dielectric response. At 730 K, the impedance spectra can be separated into two distinct regions: the high-frequency region independent of the DC bias indicative of the bulk response, and the low-frequency region which can be enhanced by increasing the bias. This fact substantially convinces that the low-frequency arc corresponds to interfacial response. However, the interfacial response is usually associated with Schottky barrier that should be depressed rather than enhanced by the DC bias. Our recently report in ZnNb$_2$O$_6$ ceramics indicated that this abnormal bias behavior was caused by sample/electrodes contacts instead of grain boundaries. This is because that the electrode is electronic conductor instead of ion conductor. When the vacancies are blocked by the interface at the electrode, they can never overcome this barrier. Thus, the DC bias notably enhances the space charge, which, in turn, enhances the Maxwell–Wagner relaxation. This finding strongly supports that $R_2$ is related to the blocked oxygen vacancies. The absence of grain boundary effect might be that fact that the BZO shows the largest grain size and its density is very close to that of single crystal [see Table 1]. This implies that the fraction of grain-boundary in BZO is very small. Thus, the influence of grain-boundary is almost negligible.

The above results indicate that $R_1$ and $R_2$ are related to bulk and interfacial effects, respectively. To further convince this point, we conduct AC conductivity analysis. Fig. 7(a) shows the AC conductivity ($\sigma(\omega)$) as a function of frequency recorded at different temperatures. We note that the curves, especially for those measured at intermediate temperatures, behave as low- and high-frequency plateaus with sigmoidal curves collecting them. The plot can be clarified into two regions (I and II) separated by a dashed line. Obviously, the well-known universal dielectric response (UDR) model fails to describe this kind of AC conductivity behavior, because the UDR conductivity is characterized by the feature of a low-frequency plateau (DC conductivity) followed by a rapid increase in the high-frequency range. To explain this behavior, we presented an equivalent circuit as illustrated in the inset of Fig. 7(a). It contains two
sintered at 1973 K for 12 h was found to show optimal dielectric properties. It was found that BZO showed incipient ferroelectric behavior in the temperature range below 420 K. Above this temperature, CDC behavior appears composed of two sets of oxygen-vacancy-related relaxations (R1 and R2). The low-temperature relaxation R1 was attributed to be a dipolar relaxation due to hopping oxygen vacancies inside grains, while the high-temperature relaxation R2 was argued to be a Maxwell-Wagner-type relaxation related to the vacancies blocked by the sample/electrode contacts.

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References


4. Conclusions

In summary, BZO powders were synthesized by solution combustion based on the glycine nitrate process. The sample

Fig. 7 (a) The frequency dependence of AC conductivity of BZO measured at different temperatures. (b) The Arrhenius plots of the conductivity with the data deduced from regions I and II as shown in (a).

\[
\sigma(\omega) = \sigma_0 + \frac{\sigma_0 - \sigma_\infty}{1 + (\omega \tau)^2}
\]

where \(\omega = 2\pi f\) is angular frequency, \(\tau\) is relaxation time, \(\sigma_0\) and \(\sigma_\infty\) are the conductivity at \(\omega = 0\) and \(\infty\), respectively. Eqn (3) is formally equivalent to the well-known Debye relaxation equation. Clearly, the AC conductivity shows a low-frequency plateau (\(\sigma_0\)) and a high-frequency plateau (\(\sigma_\infty\)) with a sigmoidal curve linking them. It was reported that the low- and high-frequency plateaus, i.e., regions I and II in Fig. 7(a), correspond to the interfacial and bulk contributions, respectively. The Arrhenius plots of \(\sigma_0\) and \(\sigma_\infty\) deduced from regions I and II, respectively, were plotted in Fig. 7(b). The activation energy for \(\sigma_0\) and \(\sigma_\infty\) was calculated to be 0.79 and 1.56 eV, respectively. These values agree well with the corresponding activation energy values for R1 and R2. This finding further demonstrates that R1 and R2 are bulk and interfacial responses, respectively.

Finally, it is worthwhile to compare the dielectric properties between pure and acceptor-doped BZO ceramics. The relaxing species in pure BZO are the inherent defects of oxygen vacancies. The observed dielectric relaxations are associated with the migration of the vacancies. Whereas the acceptor-doped BZO ceramics become the well-known proton conducting oxides. There are two distinctly important types of carriers: hydroxyl ions (OH\(^-\)) and oxygen vacancies (V\(_O\)) in the samples. These carriers are associated with the dopants, such as Y or Zr, giving rise to complex dipole pairs (OH\(^-\) – Y, OH\(^-\) – Zr, V\(_O\) – Y and V\(_O\) – Y). The high-temperature dielectric properties are thereby determined by the complex dipoles. Besides, the grain boundaries instead of the sample/electrode contacts in the acceptor-doped BZO have been widely evidenced to show higher resistance than the interior of the grains and hinder the migration of charged carriers.