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High-temperature dielectric properties of BaZr_{0.8}Y_{0.2}O_{3-δ} ceramics



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ABSTRACT

Ceramic samples of BaZr_{0.8}Y_{0.2}O_{3- δ} (BZY) were synthesized by solution combustion based on the glycine nitrate process. The dielectric properties were investigated in the temperature range of 300–870 K and frequency range of 10²–10⁶ Hz. Two types of carriers, hydroxyl ions and oxygen vacancies, coexist in the material and lead to three sets of relaxations. The activation energies were calculated to be 0.50, 0.65, and 1.27 eV for low-, middle- and high-temperature relaxations, respectively. The low-temperature relaxation was ascribed to be a dipolar relaxation resulting from the OH₀^o-Y dipole. The middle- and high-temperature relaxations associated with space charges caused by hopping oxygen vacancies blocked by grain boundaries and sample-electrode contacts, respectively.

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1. Introduction

ABO₃-type perovskite proton conducting oxides have recently attracted considerable attention because they are valuable electrolyte materials for high temperature fuel cells and hydrogen sensors [1–6]. BaZrO₃ has the highest lattice constant in the cubic perovskite structure. This high symmetry is essential for the high solubility limit of protonic defects and for high isotropic proton mobility [7], which makes BaZrO₃ an interesting parent compound for the development of proton conducting electrolytes by doping [8,9]. Yttrium-doped BaZrO₃ oxides have been demonstrated to combine high stability with high proton conductivity at temperatures below approximately 1000 K [7]. When the Y dopant was introduced into the BaZrO3 structure, a few Zr^{4+} (0.72 Å) atoms were replaced by Y^{3+} (0.90 Å), leading to oxygen vacancies due to charge compensation $(Y_2O_3 \xrightarrow{BaZrO_3} Y'_{Zr} + V_0^{\bullet\bullet} + 3O_0^{\chi})$, which in turn leads to the reactive absorption of water. According to the reaction $H_2O + V_0^{\bullet \bullet} + O_0^x \rightarrow 2OH_0^{\bullet}$ (Kröger-Vink notation has been used), two positively charged proton defects (OH_{Ω}^{\bullet}) are formed. Ydoped BaZrO₃ (BZY) is now considered to be one of the most promising materials among the perovskite proton conducting oxides [10] because it combines perfect mechanical and chemical stability with high proton conductivity [11–13].

It is well known that in the perovskite-type proton conductors exist two distinctly important types of carriers: the hydroxyl ion (OH_{0}^{\bullet}) and an oxygen vacancy $(V_{0}^{\bullet\bullet})$. Hydroxyl ions and oxygen vacancies could occupy the sites of either Y or Zr, giving rise to four types of dipole pairs (OH_0^{\bullet} -Y, OH_0^{\bullet} -Zr, $V_0^{\bullet\bullet}$ -Y, and $V_0^{\bullet\bullet}$ -Zr) in the lattice. It has been reported that the transport of an oxygen vacancy can be ignored below 873 K [14]. According to the infrared absorption spectra, the OH_0^{\bullet} -dopant dipole pair dominates the dielectric properties of the protonic oxides [7,15]. Therefore, lowfrequency (below 1 MHz) dielectric spectroscopy might be a powerful technique to investigate the dynamic proton behavior. Some dielectric studies related to Yb-doped oxides have been reported [15,16]. However, there are literally no data of the dynamic properties available for BZY ceramics. Hence, it is of great significance to characterize this material by using low-frequency dielectric spectroscopy.

In this paper, we performed investigations of the dielectric properties of BZY ceramics in the temperature range of 300–870 K. Three sets of relaxations were observed. The mechanisms of these relaxations are discussed below.

2. Experimental details

BZY samples were synthesized by solution combustion based on the glycine nitrate process. Stoichiometric amounts of barium nitrate (Ba(NO₃)₂) (0.02 mol), zirconium nitrate (Zr(NO₃)₄·5H₂O) (0.016 mol) and yttrium nitrate (Y(NO₃)₃·6H₂O) (0.004 mol) were dissolved in deionized water (800 ml) to form a solution. Glycine

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was then added at a molar ratio of glycine (0.08 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 autocombustion. The resulting primary powders were further calcined at 1373 K for 5 h in air. After cooling to room temperature naturally, pellets of 11 mm diameter and approximately 1.1 mm thickness were pressed and sintered at 1873 K for 12 h. The phase purity of the sintered pellets was characterized by X-ray diffraction (XRD) on a Rigaku SmartLab diffractometer (Rigaku Beijing Co., Beijing, China) with Cu $K\alpha$ 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.

3. Results and discussion

Fig. 1 shows the typical room-temperature XRD pattern of the BZY ceramic sample in the 2θ range of $20-80^{\circ}$. The pattern can be indexed based on a cubic structure with a *Pm-3m* space group (JCPDS file No. 06-0399) without any detectable impurity phases. The lattice parameter was calculated with UnitCell software and was found to be 4.19 Å. This value is fairly consistent with those reported (4.20 Å) in Y-doped BaZrO₃ by Kreuer et al [17]. The surface morphology of the BZY is shown on the insert of Fig. 1. It can be seen that the grain size is non-uniform. The grains, with an average size of approximately 0.5–1 µm, are densely packed together with some smaller pores (having sizes of less than 0.5 µm). The relative density is 90% of the theoretical density, as determined by the Archimedes method.

Fig. 2(a) and (b) show, respectively, the temperature (*T*) dependence of the dielectric constant, ϵ' , (the real part of the complex permittivity, ϵ^*) and the dielectric loss tangent (tan $\delta = \epsilon'' / \epsilon'$, ϵ'' is the imaginary part of the complex permittivity) for BZY at various frequencies. In Fig. 2(a), the noteworthy



Fig. 1. The XRD pattern of the BZY sample recorded at room temperature. The insert shows the SEM surface morphology.



Fig. 2. The temperature dependence of (a) the dielectric constant, ϵ' , and (b) the dielectric loss tangent, $\tan \delta$, for BZY at various frequencies.

observation is that the curves can be clarified into three regions: region I (300–450 K), region II (450–600 K), and region III (600–870 K). Correspondingly, there are three sets of relaxation peaks of tan δ . The positions of these peaks shift towards higher temperatures with increasing frequency. These results indicate that there exist three thermally activated relaxations in the sample. To discuss each relaxation clearly, the relaxations are referred to as R1, R2, and R3 in the order ascending temperature as indicated by the circles in Fig. 2(b).

As a relaxation parameter analysis is favorable for better understanding the mechanism of the observed relaxations, we, therefore, focused on the calculation of the relaxation parameters of each relaxation. In doing so, we performed dielectric measurements in a frequency domain with more detailed temperatures. Fig. 3(a)–(c) show the frequency dependence of tan δ for BZY at temperatures ranging from 315 to 675 K with temperature steps of $\Delta T = 20$ K. It is seen that, in the temperature range below 375 K [Fig. 3(a)], the spectroscopic plot shows one relaxation peak, whose position moves to a higher frequency with increasing temperature. Obviously, as the measuring temperature rises, the first appearing relaxation in the frequency spectrum can be identified to be R1 as indicated in the temperature spectrum [see Fig. 2]. At T = 375 K, there is an incipient peak at the lowest frequencies, and when temperature rises to 395 K, a second relaxation peak, corresponding to R2, appears. As a result, two relaxation peaks coexist in the spectroscopic plot in the temperature range of 395-515 K [Fig. 3(b)]. This result is similar to that found in Yb-doped SrZrO₃ [15,16] and Yb-doped SrCeO₃ [18]. Moreover, the frequency regions of the relaxation peaks (R1 and R2) in the present sample are in good agreement with those reported in the Yb-doped samples. At T = 535 K, R1 almost moves out of the measuring frequency window, and the high-frequency wing of the relaxation peak R3 appears [Fig. 3(b)]. In the temperature range of 575–675 K [Fig. 3(c)], R1 is invisible in the spectroscopic plot, but R3 appears. This plot is composed of R2 and R3. The measuring temperature and the peak position in the frequency spectrum $(f_{\rm P})$ are plotted according to the Arrhenius law:

$$f_{\rm P} = f_0 \exp(-E_{\rm a}/k_{\rm B}T) \tag{1}$$

where f_0 is the eigenfrequency, E_a is the activation energy for relaxation, and k_B is the Boltzmann constant. Arrhenius plots for R1, R2, and R3 (closed points) along with their linear fits (straight lines



Fig. 3. (a-c) Frequency dependence of tan δ for BZY at different temperatures. Fig. 3(d) Arrhenius plots of the three relaxations. The straight lines are the linear fitting results.

through the data points) are shown in Fig. 3(d). The relaxation parameters, E_a and f_0 , are calculated, respectively, to be 0.50 eV and 9.97 × 10¹⁰ Hz for R1, 0.65 eV and 1.28 × 10¹¹ Hz for R2, and 1.27 eV and 1.27 × 10¹³ for R3.

The activation energy value for R1 (0.50 eV) is comparable with the typical value of approximately 0.55 eV for relaxations caused by proton-dopant associations [15,16,19]. Kamishima et al. [15] has argued that this relaxation is ascribed to the OH_0^{-} -Yb dipole in Yb doped-SrZrO₃. Since Y³⁺ has similar ionic radii as Yb³⁺ and they all locate at the center of the octahedron, the R1 in Y-doped BaZrO₃ can thus be reasonably ascribed to be a dipolar relaxation resulting from the OH_0^{-} -Y dipoles.

We then focused on the mechanisms of R2 and R3. Their activation energies are located in the range of 0.6-1.2 eV for oxygenvacancy-related relaxations [20], indicating that these relaxations might be associated with oxygen vacancies. Nevertheless, as already noted, the transport of an oxygen vacancy can be ignored below 873 K [14]. This implies that the oxygen-vacancy hopping motion induced polaron relaxation can be ignored in the tested temperature window. However, it has been widely shown that grain boundaries are characterized by higher resistance values than the interior grains and hinder the migration of charged carriers (oxygen vacancies and/or prontons) [21-23]. When the carriers are blocked by the boundaries, space charge occurs therein. In light of this fact, a Maxwell-Wagner relaxation related to the grain boundaries might be observed by impedance spectroscopy. We, therefore, performed an impedance analysis, as it is a powerful technique to detect the dielectric contributions from the bulk, grain boundary, and contact effects. Fig. 4(a) displays the complex impedance plots of the BZY ceramic sample measured at 335 K. The Nyquist plot (Z' versus Z'', where Z' and Z'' are the real and imaginary parts, respectively, of the complex impedance, Z^*) consists of two inconspicuous parts: smaller and larger arcs in the high- and low-frequency regions, respectively. This indicates that there are two main dielectric contributions from the bulk or grain (the high-frequency arc) and the grain boundary (the lowfrequency arc) at the measuring temperature. The low-frequency grain boundary contribution is associated with the Schottky barrier [21–23] that can be tuned using a dc bias. Nyquist plots for 475 K under different dc biases, ranging from 0 to 40 V (corresponding to a field of 0–363.6 V/cm), are plotted in Fig. 4(b). It is clearly seen that the low-frequency arc can be depressed by a dc bias, whereas the high-frequency arc is bias independent, which is indicative of the bulk contribution. The high-frequency arc can be well fitted with the Zview software [24] using an equivalent circuit consisting of a resistor (R_g) and a constant-phase element (CPE) as shown on the inset of Fig. 4(a). The impedance of the CPE is described by:

$$Z_{CPE}^* = 1/A(j\omega)^n \tag{2}$$

where ω is the angular frequency, and *A* and $n(0 \le n \le 1)$ are adjustable parameters dependent upon the temperature. The fitted result for the data in Fig. 4(a) is given in the inset of this figure. The value of R_g was calculated to be $4.83 \times 10^6 \Omega$, which was found to decrease rapidly with increasing temperature. For example, when T = 675 K, R_g was reduced to a value of 650 Ω . This value is much smaller than that of the grain boundary, indicating that the grain boundary contribution will prevail over the grain contribution at a higher temperature. To confirm this inference, Fig. 4(c) displays the complex impedance plots of the BZY ceramic sample under different temperatures ranging from 675 to 775 K. It is seen that



Fig. 4. (a) Nyquist plot of the BZY sample measured at 335 K. The insert of Fig. 4(a) displays the equivalent fitting circuit and the fitting result of the high-frequency arc. (b) Nyquist plot of the BZY sample measured at 475 K under various dc biases. (c) Nyquist plot of the BZY sample at select temperatures. (d) Representation of Z' versus |Z''|/f at 775 K. The linear linear lines are guides for the eye.

with increasing temperature, the low-frequency arc develops into a full semicircle and becomes the predominant part of the Nyquist plot. The grain-related semicircle can be neglected. Based on the above results, it follows that R2 is ascribed to the grain boundary response.

It is worth pointing out that, apart from the grain boundaries, the electrode-sample contact also involves the Schottky-type barrier due to the difference of the Fermi level between the sample and the electrode. Likewise, the dc bias can depress the dielectric response from the electrode-sample contact. However, it is frequently hard to completely separate the contributions of the grain boundary and the electrode-sample contact in the Nyquist plot if they possess close relaxation times. In this case, an alternative presentation of Z' versus Z''/f was used. This presentation was been proven to be much more effective in identifying the dielectric contributions resulting from different parts in terms of the three straight lines from low to high frequencies corresponding to the dielectric responses from the contact, grain boundary, and bulk [25,26]. Fig. 4(d) shows such a plot of the same data measured at 775 K in Fig. 4(b). It can be seen that there are three sectional linear lines marked as A, B and C corresponding to the grain, boundary grain, and contact, respectively. The contact contribution is well separated from the grain boundary contribution. Moreover, the contact contribution region (contact frequency) decreased with decreasing temperature. For example, the frequency is 253 Hz at 775 K, which then decreased to 120 Hz at 735 K. This indicates that the contact-related dielectric response is at work in the low frequency range at higher temperatures. Hence, R3 is ascribed to the contact response.

To further confirm the contact origin of R3, we conducted an ac conductivity analysis. The ac conductivity (as a function of frequency) that was recorded at different temperatures in the frequency range of 100 Hz to 1 MHz is shown in Fig. 5. One notes that in the low-frequency range, the ac conductivity increased as a result of the electrode conductivity [27], i.e., it shows a flat value followed by a rapid increase. This behavior can be described by the universal dielectric response (UDR) [28]:

$$\sigma(T,f) = \sigma_{\rm dc} + A(T)f^{\rm s} \tag{3}$$

where σ_{dc} is the dc conductivity, and A(T) and s(0 < s < 1) are



Fig. 5. Frequency dependence of the ac conductivity of the BZY sample measured at different temperatures. The inset shows the Arrhenius plots of the dc conductivity.

temperature-dependent constants. The dc conductivity, shown on the inset of Fig. 5, follows the Arrhenius law:

$$\sigma_{\rm dc} = \sigma_0 \exp(E_{\rm dc}/k_{\rm B}T) \tag{4}$$

where E_{dc} is the activation energy of the conductivity, and σ_0 is the pre-exponential factor. A linear fit, shown as a straight line on the inset, yields $E_{dc} = 1.06$ eV. This value is comparable with the activation energy value of the relaxation of R3 (1.27 eV) and agrees well with that of the oxygen-vacancy hopping conduction process [20]. This further confirms that R3 is linked with the oxygen-vacancy hopping process. Upon an applied electric field, the hopping oxygen vacancies will finally be blocked by the electrode/sample contact. Since the electrode is an electron conductor instead of an ion conductor, the vacancies, therefore, accumulate in a thin layer next to the electrode, which leads to electrode polarization [29]. As a result, the value of the activation energy of relaxation (E_a =1.27 eV) is relatively higher than that of the conduction

process. Therefore, it is the contact that blocks the hopping oxygen vacancies giving rise to the relaxation of R3.

Finally, it is worth pointing out that the ac conductivity isotherms deviate from the UDR behavior at the highest frequencies because they show a gentle increase. This is simply the characteristic feature of ionic conductivity, which can be described by the concept of the mismatch and relaxation model [30,31].

4. Conclusions

In summary, the dielectric properties of BZY were investigated in the temperature range of 300–870 K and the frequency range of 10^2-10^6 Hz. The sample showed three sets of relaxations (R1 to R3 in the order of ascending temperature) in the measured temperature range. R1 was ascribed to be a dipolar relaxation resulting from the OH₀⁻-Y dipoles. The R2 and R3 relaxations were argued to be Maxwell-Wagner-type relaxations caused by oxygen vacancies blocked by the grain boundaries and sample/electrode contacts, respectively. These results may be helpful for better understanding the dynamics of the charged defects, especially the behavior of protons and oxygen vacancies in ABO₃-type perovskite proton conducting oxides.

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