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IMPEDANCE STUDIES ON THE SUB-MICRON GRAIN Yb-DOPED Ba(Ce,Zr)O_3 CERAMICS AT INTERMEDIATE TEMPERATURES

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ABSTRACT

A ceramic of $Ba(Ce_{0.6}Zr_{0.4})_{0.95}Yb_{0.05}O_{2.975}$ was prepared by the Pechini method. Morphology of the fractured surface of sintered pellet was observed using a scanning electron microscope. The sample formed clear and compact grains with submicron sizes. Impedance data were collected using a high frequency response analyzer under wet hydrogen in the temperature range from 200 to 800 ^{o}C. At $T \leq 250$ ^{o}C, the high frequency arc corresponding to grain response, the mid-frequency arc due to the grain boundary response, and low frequency arc attributed to the electrode/electrolyte interface were observed. Above 300 ^{o}C, the grain resistance was obtained from the intercept of the grain boundary arc with the real axis at high frequency. It was also noticed that above 300 ^{o}C, the *Z*-imaginary data at high frequencies changed its sign to positive values. All the responses were resolved by the fitting procedure using an equivalent circuit representing the brick-layer model. Arrhenius plot of proton conductivity and capacitances associated with the grain and grain boundary of $Ba(Ce_{0.6}Zr_{0.4})_{0.95}Yb_{0.05}O_{2.975}$ are also presented.

Keywords: Ba(Ce,Zr)O_3; microstructure; impedance;

INTRODUCTION

Acceptor doped ceramics perovskite based on cerates and zirconates exhibit high conductivity varies from ionics or/and electronic conduction depending on the dopant elements, measuring atmospheres and operating temperatures [1-3]. Most of the electrical conductivities have been studied using a.c impedance spectroscopy. The technique is capable to separate several responses inside the sample such as grain, grain boundary and electrode/electrolyte interface. However in most cases, the obtained impedance spectrum deviated from the ideal spectrum due to overlapping arcs in *Z'* and *Z"*-plane. A detail literature review shows that different interpretation of the impedance spectrum came out from the studies even though the brick-layer model was used. For example, Potter and Baker [4] reported that for $SrCe_{0.95}Yb_{0.05}O_3$, bulk and grain boundary conduction cannot be measured separately at temperature above 300 ^{o}C in frequency ranging from 0.01 Hz to 32 MHz. However, Slade et al. [5] claimed that the bulk response of Y-doped $BaZrO_3$ can be resolved at temperature up to 960 ^{o}C with the geometrical capacitance, $C_g \approx 140$ nF. Therefore, we can conclude that the impedance analysis still suffer from a certain amount of ambiguity in this high conducting ceramics. To overcome the problem, several procedures can be taken in impedance analysis not only for cerates and zirconates compounds but also in other types of ceramics. The considerations are listed as follows; (i) by observing the evolution of impedance spectra at low temperature (100 ^{o}C) [6] (ii) by taking into account the capacitance of each response since every response has its own range of capacitance values [7] (iii) by comparing the impedance spectra between single crystals and polycrystalline [6] (iv) by varying the thickness of sample [8] .

In this work, we systematically analyzed the impedance spectrum by considering the procedures (i) and (ii) for the $Ba(Ce_{0.6}Zr_{0.4})_{0.95}Yb_{0.05}O_{2.975}$ sample in atmosphere containing wet hydrogen.

EXPERIMENT DETAILS

A detail preparation for the powders of $Ba(Ce_{0.6}Zr_{0.4})_{0.95}Yb_{0.05}O_{2.975}$ was reported elsewhere [9]. The calcined powder was pressed to become a pellet with 13 mm in diameter and 2 mm thickness. The pellet was sintered at 1450 ^{o}C in air for 6 h. For impedance conductivity measurement, Pt paste (Engelhard) was painted onto opposite surfaces of the pellet as electrodes. The coated pellet was heated at 1000 ^{o}C in air for 5 h. The impedance of the sample in wet hydrogen was measured using a High Frequency Response Analyzer (HFRA), Solartron 1260. Wet hydrogen was produced by bubbling the hydrogen gas through deionized water at room temperature. Before the measurement, the sample was heated in the desired atmosphere at 700 ^{o}C for 24 h. Impedance spectra were recorded from 200 to 800 ^{o}C in steps of 50 ^{o}C. The frequency was swept from 1 Hz to 10 MHz and a 500 mV a.c. signal was applied to the sample. The impedance spectra were analyzed to extract the grain and grain-boundary responses using a Z-View program (Scribner Associates, Inc).

RESULTS AND DISCUSSION

Figure 1 shows Nyquist plots for the sample at 200, 400 and 700 ^{o}C. At 200 ^{o}C, the high frequency arc corresponds to grain response and the mid-frequency arc is associated to the grain boundary response. The third arc is attributed to the electrode/electrolyte interface. Impedance spectra revealed that the grain semicircle was observed only at $T \leq 250$ ^{o}C. All the responses were resolved by the fitting procedure using an equivalent circuit representing the brick-layer model. Up to 250 ^{o}C, the equivalent circuit consists of a combination of three parallel pairs of resistor-constant phase element in series. Above 300 ^{o}C, the grain resistance (R_g) was obtained from the intercept value of the grain boundary arc with the real axis at high frequency. However, the R_g data points were found to deviate from the linearity of Arrhenius behavior. Thus, only total conduction was discussed in this study. It was also noticed that above 400 ^{o}C, the *Z*- imaginary data at high frequencies change its sign to positive values. The effect was due to the presence of inductive element caused by the experimental set-up [10]. As temperature increased, the inductive effect became dominant due to the smaller specimen resistance compared with the input impedance of the analyzer. This artifact limits the capability of Solartron 1260 frequency response analyzer at 32 MHz.

The relation of $C = Y^{1/n} R^{(1/n - 1)}$, where *R* is the resistance and *Y* and *n* is the parameters associated with the constant phase element (CPE), was used to calculate the capacitance value. Table 1 shows the geometrical capacitance value for the grain (C_g) and grain boundary (C_{gb}) responses of $Ba(Ce_{0.6}Zr_{0.4})_{0.95}Yb_{0.05}O_{2.975}$ at selected temperatures (*T*). The identification of the first semicircle as bulk response based on the extracted capacitance was in the order of 10^{-12} to 10^{-11} farad. The capacity of the second semicircle was of the order of several nanofarad and corresponds to the grain boundary [4].

Table 1: Geometrical capacitance value for grain and grain boundary responses

T (°C)	C_g (F)	C_{gb} (F)
200	2.1×10^{-11}	1.2×10^{-9}
250	2.4×10^{-11}	1.3×10^{-9}
400	-	0.8×10^{-9}
550	-	0.3×10^{-9}
600	-	0.4×10^{-9}

As mentioned earlier, the reported works claimed that grain semicircle could not be measured at temperature above 300 °C. The stated temperatures higher than that obtained from this study may be due to the different grains size of sample. It is known that WCMs produced smaller grains compared to that prepared by SSR. As a result, the grain boundary semicircle tends to overwhelm grain semicircle compared to that of bigger grain. Morphology of the sub-micrometer grain is shown in the insert in Figure 2. The evolution of impedance diagram as a function of grain size was also discussed by Tadokoro et al. [11] for CeO_2-8 mol% Y_2O_3. From the analysis of impedance spectrum, the grain boundary resistance gave a higher contribution to the total resistance of samples. However, the sample still maintained high proton conductivity in wet hydrogen and its values were found to be comparable to that prepared by SSR [12] as shown in Figure 2.

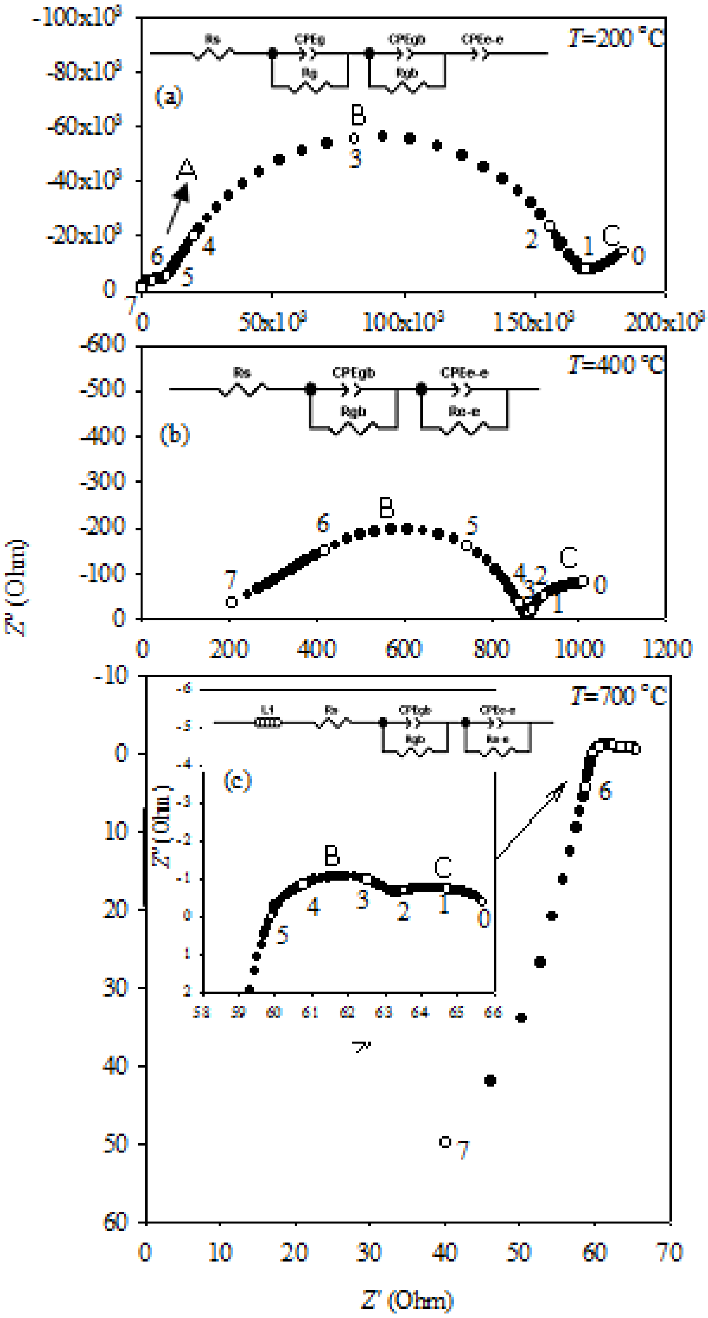

Figure 1: The impedance spectrum of $Ba(Ce_{0.6}Zr_{0.4})_{0.95}Yb_{0.05}O_{2.975}$ at 200, 400 and 700°C in wet hydrogen (number 0 to 7 is n value for 10^n in the frequency range of impedance measurement). A, B and C are the responses associated to the grain, grain boundary and electrode/electrolyte interface, respectively

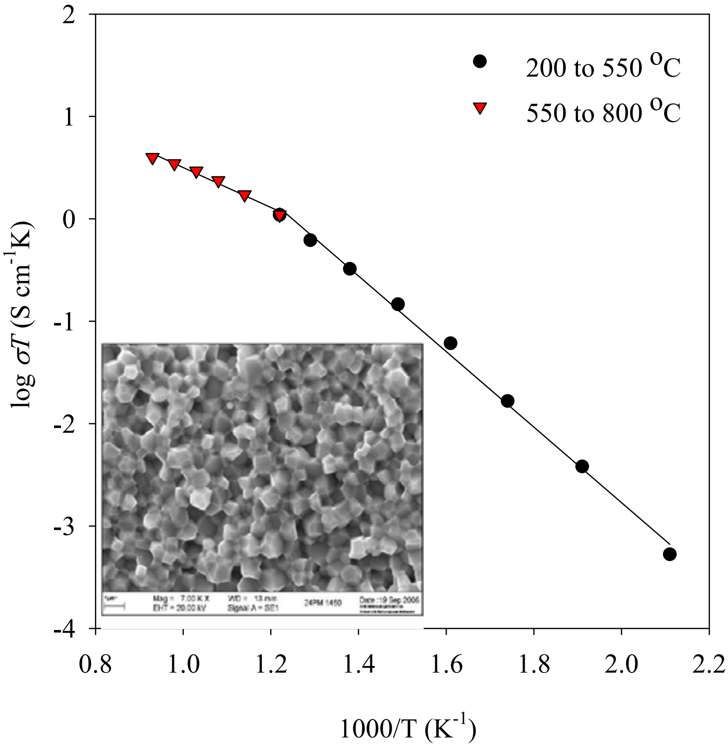

Figure 2: The σT values of $Ba(Ce_{0.6}Zr_{0.4})_{0.95}Yb_{0.05}O_{2.975}$ as a function of temperature in wet hydrogen (*insert* is SEM micrograph showing the microstructure of the fracture surface of pellet sintered at 1450 ^{o}C)

CONCLUSION

Impedance analysis showed the sub-micron grain response could only be observed at $T \leq 250$ ^{o}C. This phenomenon limits the grain resistance (R_g) data and it was found that the R_g data points deviated from the linearity of Arrhenius behaviour. Thus, only total conduction was discussed in this work. Analysis of impedance spectrum also showed the grain boundary resistance gave a higher contribution to the total conduction of samples.

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