

ELECTRICAL PROPERTIES OF Ba(Ce,Zr)O₃ SOLID SOLUTION PREPARED BY A TWO- STEP SINTERING METHOD

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ABSTRACT

A single perovskite-phase of BaCe_{0.54}Zr_{0.36}Y_{0.1}O_{2.95} (BCZY) solid solution was successfully prepared by a sol-gel method. The powder was compacted using hydraulic press and sintered using a two-step sintering (TSS) method at T₁=1500 °C and T₂=1450 °C with respective 25 °Cmin⁻¹ and 50 °Cmin⁻¹ heating and cooling rates. Electrical conductivity of the sintered pellet was measured in air using an impedance spectroscopy at temperature in the range of 200-800 °C. Impedance results showed that the grain semicircle was only observed at T=200 °C and 250 °C with capacitance values associated to grain and grain boundary were 10⁻¹¹ F and 10⁻⁹ F, respectively. All the responses were resolved by a fitting procedure using an equivalent circuit based on the brick- layer model. Electrical conductivity of the sample in air at T= 500 °C was 3.13x10⁻⁴ Scm⁻¹.

Keywords: BCZY; TSS; electrical conductivity

INTRODUCTION

Perovskite-type oxides have generated tremendous interest because of their potential applications in hydrogen-related electrochemical devices, which is mainly due to their high proton conductivity in hydrogen containing atmosphere at intermediate temperature range (450–750 °C) [1]. Perovskite-type cerates especially BaCeO₃ with the highest protonic conductivity among all developed proton conductors, is deemed to be the most promising candidate, but its chemical stability against H₂O and CO₂ is relatively poor. However, partially substitution of Ce with Zr in BaCeO₃ leads to a significant improvement in the thermochemical stability although it will also cause a decrease in the protonic conductivity due to the increase in the activation energy for proton transport. Nevertheless, as a tradeoff between the high proton conductivity of BaCeO₃ and the high thermochemical stability of BaZrO₃, a number of solid solutions of BaCeO₃ and BaZrO₃ to become Ba(Ce,Zr)O₃ have been investigated in many reports

[1-7].

Recently, Y-doped $\text{BaCe}_{0.54}\text{Zr}_{0.36}\text{Y}_{0.1}\text{O}_{2.95}$ solid solution have been widely investigated as a candidate of proton conductor with combined better chemical stability and electrical conductivity. This material exhibits higher conductivity at relatively low temperature in comparison to yttria- stabilized zirconia (YSZ) electrolytes, which could make them as a suitable alternative to IT-SOFC. Further investigations towards enhancing the conductivity of $\text{BaCe}_{0.54}\text{Zr}_{0.36}\text{Y}_{0.1}\text{O}_{2.95}$ (BCZY) electrolyte has shown that the reducing grain size can also be effective [8]. Most ceramic materials are synthesized by a conventional step sintering (CSS) method. But this technique can only produce dense sample with bigger grain size ($>1\text{ }\mu\text{m}$) [9]. Furthermore, compared with the CSS method, two step sintering (TSS) method also shown more positive vibes to the distribution of ceramic microstructure [10]. It provides a cost effective path to prepare fine-grain and homogeneous microstructure ceramics as reported by J.Ding et al., [8] for sample $\text{BiNaTiO}_3\text{-BaTiO}_3\text{-KNaNbO}_3$.

EXPERIMENTAL

A detail preparation of single-phase sample in form of powder was described elsewhere [11]. The powder was compacted by a Specac's Atlas Series Manual Hydraulic Press into disc 13 mm in diameter and 1-2 mm thickness. The pellet was sintered by a TSS method at $T_1=1500\text{ }^\circ\text{C}$ and subsequently continued by $T_2=1450\text{ }^\circ\text{C}$. The holding time for T_1 was 1 min and the dwell time for T_2 was 720 min. The applied heating and cooling rates was $25\text{ }^\circ\text{Cmin}^{-1}$ and $50\text{ }^\circ\text{Cmin}^{-1}$, respectively. Both side of the pellet surfaces were manually painted by platinum (Pt) ink and heated at $1000\text{ }^\circ\text{C}$ for 120 min to get a good contact between electrode (Pt) and electrolyte (BCZY). Impedance spectra were recorded in the frequency range of 42 Hz to 1 MHz by a HIOKI 3532-50 LCR HiTESTER impedance analyzer. Two platinum wires were connected to the fabricated cell of Pt|BCZY|Pt. The measurement was performed at $200\text{-}800\text{ }^\circ\text{C}$ in air with $50\text{ }^\circ\text{C}$ time interval. The impedance spectra were analyzed to extract the grain (g) and grain boundary (g_b) responses using a ZIVE Z-MAN 2.2 program.

RESULTS AND DISCUSSION

Figure 1 shows the representative Nyquist plots obtained from BCZY pellet in air after sintered by a TSS method. Impedance measurement revealed that the grain semicircle was only observed at $T=200\text{ }^\circ\text{C}$ and $250\text{ }^\circ\text{C}$. Above $300\text{ }^\circ\text{C}$, the first semicircle gradually became smaller and disappeared as the temperature increased. Therefore, the high frequency intersection of Nyquist-plot with Z' axis is taken as the grain interior resistance (R_g). All the responses were resolved by the fitting procedure using an equivalent circuit representing the brick layer model [12]. Up to $500\text{ }^\circ\text{C}$, the equivalent circuit consists of a combination of two sub-circuits of parallel resistor-constant phase elements (Q) in series as shown in the insert Figure 1. The sub-circuits were represented to grain ($R_1\text{-}Q_1$), grain boundary dispersion ($R_2\text{-}Q_2$) and the electrode/electrolyte interface ($R_3\text{-}Q_3$) responses.

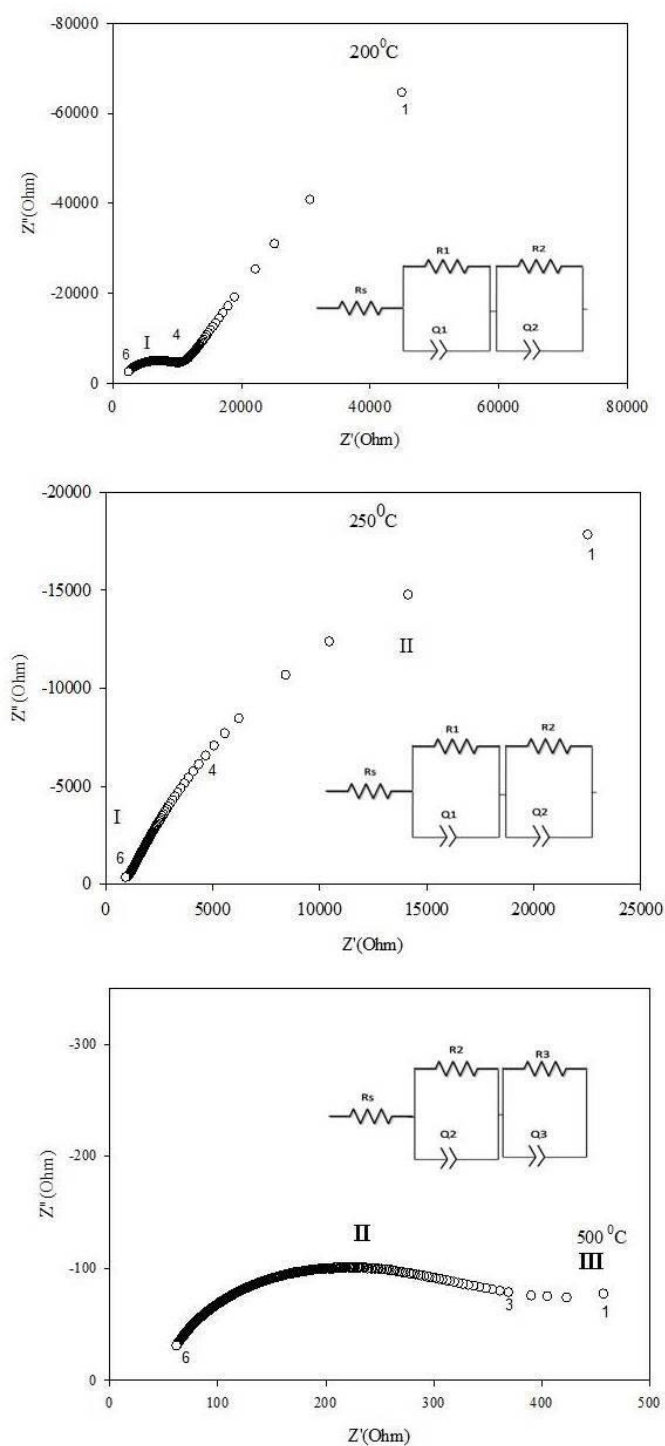


Figure 1: Impedance spectrum of BCZY sample prepared by a TSS method at 200 °C, 250 °C and 500 °C in air (number 1 to 6 is n value for 10^n in the frequency range of impedance measurement). I, II and III are responses associated to the grain, grain boundary and electrode/electrolyte interface, respectively.

Table 1 shows the geometrical capacitance value for the grain (C_g) and grain boundary (C_{gb}) responses of BCZY at selected temperature (T). The first semicircle or high frequency arc was identified as grain response based on its capacitance value in the order of 10^{-12} - 10^{-11} F , and the second semicircle was associated to the grain boundary response due to the capacitance value that in the range of 10^{-9} - 10^{-8} F as reported by N.Osman et al., [13] and K.D Kreur [14].

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

T (°C)	C_g (F)	C_{gb} (F)
200	6.25×10^{-11}	6.30×10^{-9}
250	1.59×10^{-11}	7.56×10^{-9}
300	-	8.20×10^{-9}
400	-	9.29×10^{-9}
500	-	9.99×10^{-9}
600	-	3.30×10^{-8}

From the analysis of the impedance spectrum, R_g data point was found to deviate from the linearity of Arrhenius behavior. Thus, only total conductivity (σT) of samples was discussed in this study. With the increased temperature, the total conductivity of the sample also increased. A comparison of total conductivity of BCZY sample with another work is presented in Table 2. Since the measurement was done in the air containing atmosphere, the electrical conductivity in proton conductor electrolyte will be leads by holes in oxidizing conditions as represented in Eq.1. Furthermore, the oxygen vacancies also influence the oxygen ion to jump from one site to another site consequently produces oxygen ion conductivity. Therefore, the low conductivity obtained in this study may due to the low mobility of holes and oxygen ion in the prepared sample. Thus, we expected that TSS method has the ability to create a sample's microstructure that retard the mobility of these two types of ions. Further works on the electrical properties of sample in water vapor and hydrogen containing atmospheres are in progress and will be reported elsewhere.

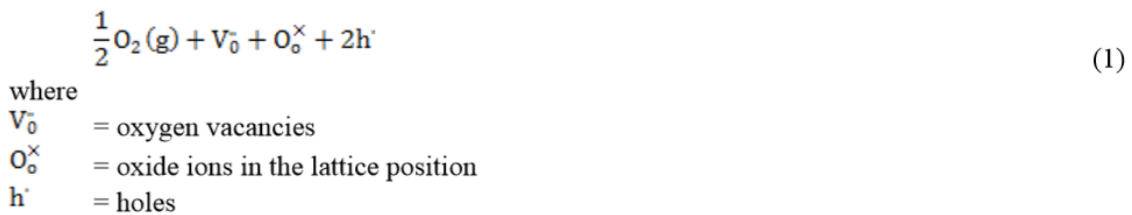


Table 2: Comparison of total conductivity for BCZY in air

Compound	σT at 600 °C in air (Scm^{-1})	Sintering Method	Reference
BaZr _{0.5} Ce _{0.3} Y _{0.2} O _{3-d}	2.5×10^{-2}	CSS	[15]
BaCe _{0.54} Zr _{0.36} Y _{0.1} O _{2.95}	6.7×10^{-4}	TSS	This work

Table 3 shows a comparison of the activation energy (E_a) of BCZY samples prepared by TSS and CSS method. The E_a of the TSS sample was found to be 0.76 eV calculated from the gradient of Arrhenius plot in Figure 2 and almost the same with the sample prepared by CSS method. Therefore, in air atmosphere, electrical conductivity of the sample prepared by TSS method is still dominated by holes, oxygen vacancies and oxygen ion species as similar to one prepared by CSS method.

Table 3: Comparison of E_a for BCZY in air at different sintering routes

Compound	E_a (eV)	Sintering method	Reference
Ba(Ce _{0.15} Zr _{0.5}) _{1-x} Y _x O _{3-d}	0.75	CSS	[16]
BaCe _{0.54} Zr _{0.36} Y _{0.1} O _{2.95}	0.76	TSS	This work

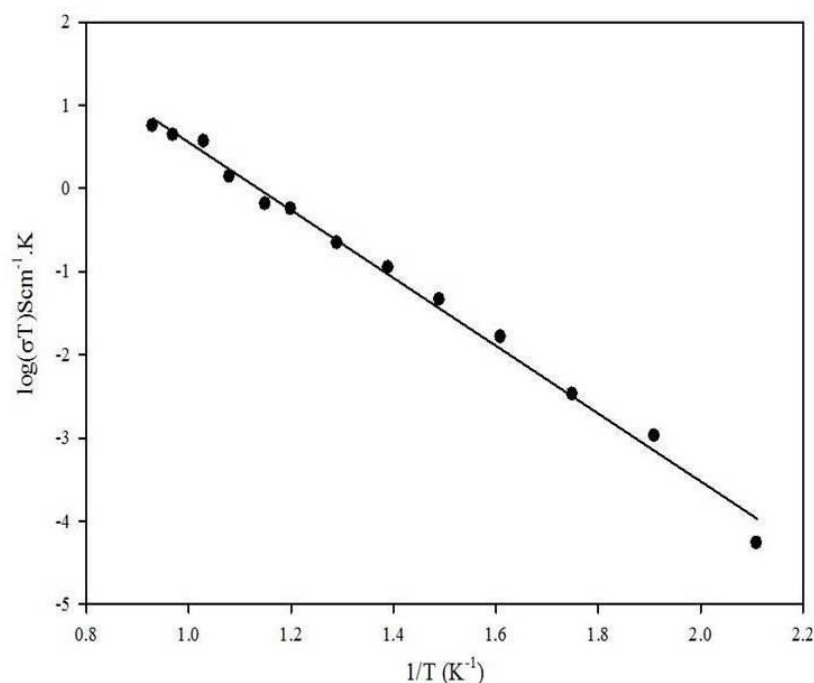


Figure 2: Total conductivity of BCZY prepared by TSS method as a function of temperature in air

CONCLUSION

Impedance analysis showed that the sub-micron grain response can only be observed at T=200 °C and 250 °C. The electrical conductivity of the sample in air at 500 °C was $3.13 \times 10^{-4} \text{ Scm}^{-1}$. It is expected that TSS method is able to retard the conduction of holes, oxygen vacancies and oxygen ion in BCZY proton conductor. Further works on the conductivity of samples in different atmosphere are still in progress and will be reported elsewhere.

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