

THE EFFECTS OF ZnO ADDITION ON THE PROPERTIES OF Y³⁺ DOPED BaZrO₃ PREPARED BY PECHINI METHOD

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ABSTRACT

A BaZr_{0.95}Zn_{0.05}Y_{0.1}O_{3- α} (BZY10) sample was successfully prepared by Pechini method (PM) using metal nitrate-salts. The properties of the synthesized powder were determined using X-ray diffraction (XRD), scanning electron microscope (SEM), particles size analyzer and Fourier transform infrared (FTIR) Spectroscopy. FTIR analysis showed that decomposition of powder almost completed at 1100 °C. Single phase of BaZrO₃ was observed after calcination at $T= 1300$ °C which is 200 °C lower than that prepared by conventional solid state reaction (SSR) method. The loose particles size obtained from SEM and particle size analyzer was in the range 30–80 nm. The conductivity of the sample was 6.9×10^{-4} S cm⁻¹ at $T= 700$ °C in wet-nitrogen and the total activation energy, E_{aT} was 0.79 eV.

INTRODUCTION

The rare earth doped BaZrO₃ proton conductor has attracted much attention as an electrolyte for intermediate temperature Solid Oxide Fuel Cells (SOFC), because it shows high chemical stability in an atmosphere containing CO₂ [1] as well as high proton conductivity in an intermediate temperature range [2]. Yttrium has been selected as the dopant because Y³⁺ doped BaZrO₃ shows high proton conductivity among other dopant [3]. The commonly used method is solid state reaction (SSR) which needs high calcination and sintering temperatures. A dense BaZrO₃ ceramic was achieved by sintering at very high temperature e.g 1700 °C [4, 5]. To overcome the problems of SSR, a wet chemical method (WCM) was used in this study. In order to improve the density of the BaZrO₃ materials, zinc was added as an additive as reported by Haile et al. (2005) [6]. Metal nitrates salts were used as precursors rather than the conventionally employed carbonates or oxides because metal nitrates have more favorable decomposition kinetics compared to their carbonate counterparts [7–9].

METHODOLOGY

The BZY10 was synthesized using the following precursors: Ba(NO₃)₂ (R&M Chemicals, 99.0% purity), Y(NO₃)₃ 6H₂O (Aldrich, 99.9% purity), Zn(NO₃)₂ 6H₂O (Fluka, 99.0% purity), and ZrO(NO₃)₂ xH₂O (Acros Organics, 99.5% purity), where $x = 4.8385$. Citric acid (Chempur, 99.0% purity), in a 1:3 and ethylene glycol (Aldrich, 99.0% purity) in a 2:3 molar ratio with respect to the total amount of cations. Citric acid

acted as a complexing agent and ethylene glycol aided the polymerization process. Stoichiometric amounts of metal nitrate salts were dissolved in deionized water to make nitrate solution with a constant stirring. Citric acid was first added into nitrate solution then ethylene glycol was gradually added under constant stirring. The pH of the resulting solution was adjusted to 7–8 by adding appropriate quantities of NH_3 and continuously stirred for 4–5 hours. The mixture was heated until a brown viscous solution or gel appeared. The gel then was heated at temperature 120–260 °C until a brown gas (known as NO_x) was released and the solution became a dark brown gel. The gel was further dried until it became a black sponge. The sponge was pre-calcined at $T=350$ °C for $\frac{1}{2}$ h, then $T=550$ °C for $\frac{1}{2}$ h and finally $T=750$ °C for $\frac{1}{2}$ h. The powder was calcined at $T=1100$ °C for 36 h and then at $T=1300$ °C 12 h. A detail sample preparation was reported in our previous work [10]. The single-phase powder was pressed to form a pellet (13 mm in diameter and 1.2 mm thickness) and sintered at $T=1500$ °C for 12 hours. The pellet surfaces were coated with platinum paste, then fired at $T=1000$ °C for 10 hours to ensure a good ohmic contact between the sample and Pt-electrode.

The powders obtained after heat treatment at $T=1100$ °C for 36 h were analyzed to detect the presence of carbonate ions using Fourier Transform Infra Red (FTIR) analyzer model Nicolet 380 (Thermo Electron Corporation). About 0.5–1 mg of the powder was dispersed in 200 g potassium bromide (KBr) and then pressed into a transparent pellet. The pellet was subjected to the infrared light and the percentage of light transmittance (%T). Phase identification of the calcined powder of the sample were determined using X-ray diffraction (XRD) Siemens model D5000 (Cu- K_α ; $\lambda = 1.5418$ Å from 20° to 80° in steps of 0.40°. Morphology of the calcined powder was observed using SEM model Leo VP and particle size distribution analyzer model Melvern Nano S (ZEN 1600). Electrical conductivity measurement was carried out using Solartron 1260 frequency response analyzer in wet-nitrogen atmosphere. The measurement was held in temperature 200 to 700 °C in steps of 50 °C. The applied voltage is 500 mV and the frequency range is 1 Hz to 10 MHz.

RESULTS AND DISCUSSION

Fourier transforms infrared (FTIR) Spectroscopy

Figure 1 shows the FTIR spectrum of the powder obtained after calcination at 1100 °C for 36 h. A broad band appears at around 3435 cm^{-1} corresponding to the presence of water and hydroxyl group. The twin peak around 2341 cm^{-1} is attributed to the artefact from instrument. Even after calcined at 1100 °C for 36 h the trace of carbonate compound (CO_3^{2-}) residue still present in the sample as shown by the small peaks at 1456 cm^{-1} and 855 cm^{-1} [11]. This observation is in good agreement with the results of TG/DTG as reported previously [10]. The large vibration band observed around 537 cm^{-1} in the calcined powder is due to Zr-O vibration in the perovskite structure.

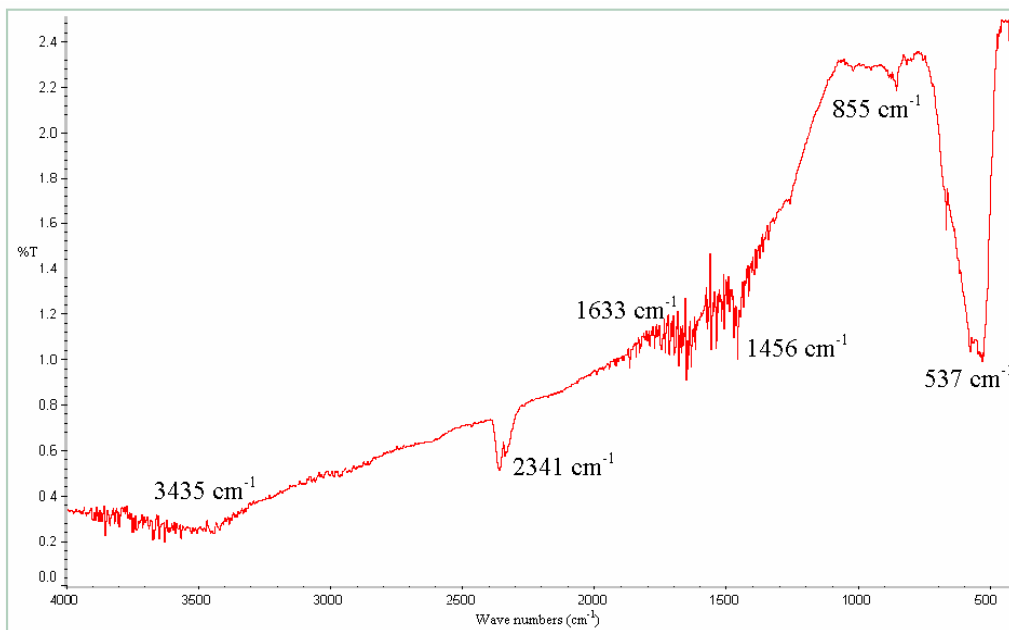


Figure 1: FTIR spectrum of BZY10 of calcined powder at $T= 1100\text{ }^{\circ}\text{C}$ for 36h

Scanning Electron Microscope (SEM)

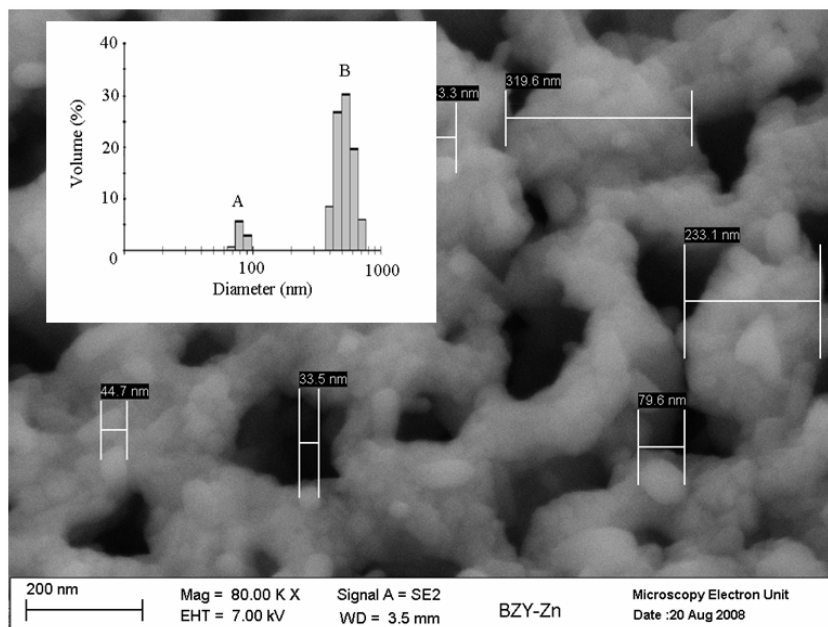


Figure 2: SEM image of the powders obtained after calcined at $T= 1100\text{ }^{\circ}\text{C}$ for 12h (insert is particle size distribution calcined at $T= 1100\text{ }^{\circ}\text{C}$ for 12h)

Figure 2 shows the morphology of BZY10 powder calcined at $T=1100\text{ }^{\circ}\text{C}$ for 12 h. The particles are spherical in shape and the loose particles size lies in the range 30–80 nm. The agglomerates characterized by diameter 200–400 nm from the SEM. However, the agglomerates size that shown in particles size distribution in range 300–800 nm as shown in Figure 2 (*insert*). The bimodal distribution of the particle size obtained in this work was smaller to that reported by Taglieri et al. [12] for the sample of BaZrO_3 prepared via citrate route. They reported that the sample calcined at $T=700\text{ }^{\circ}\text{C}$ for 3 h have two groups of particles lying between 60 μm and 4 μm (80 %) and about 10 % in the 2 μm in range.

(3.3) X-Ray Diffraction (XRD)

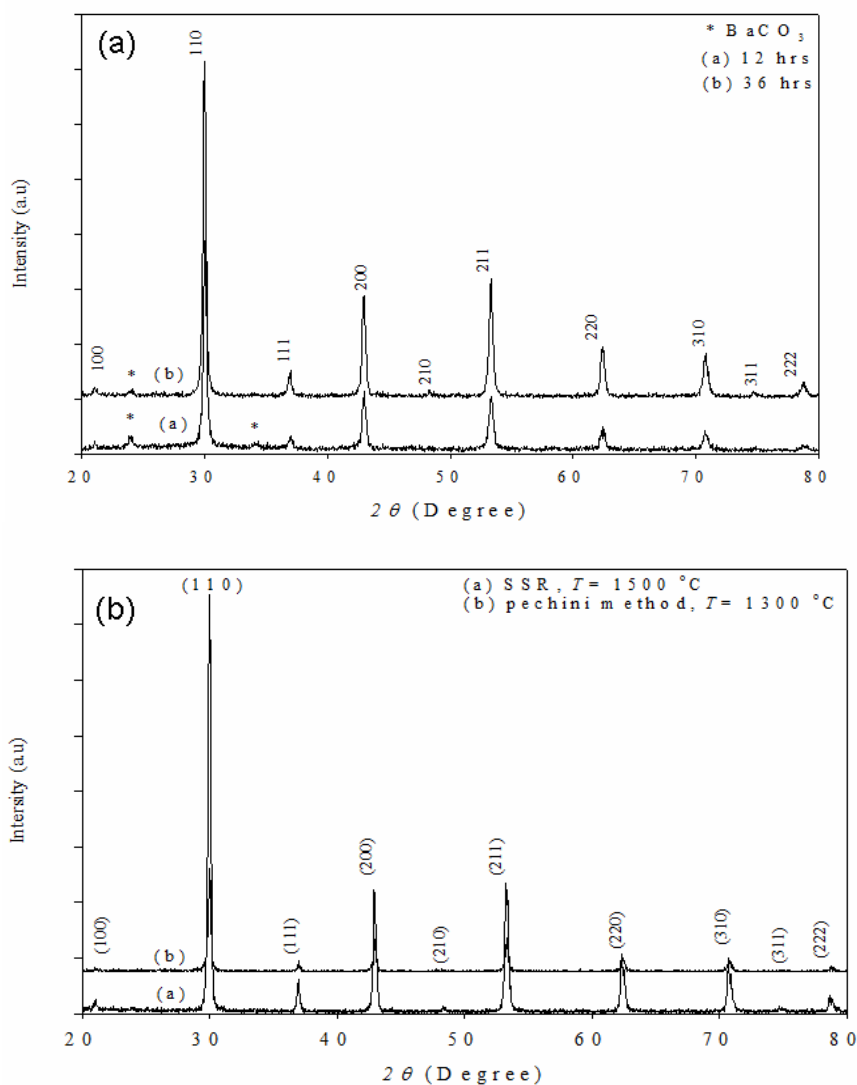
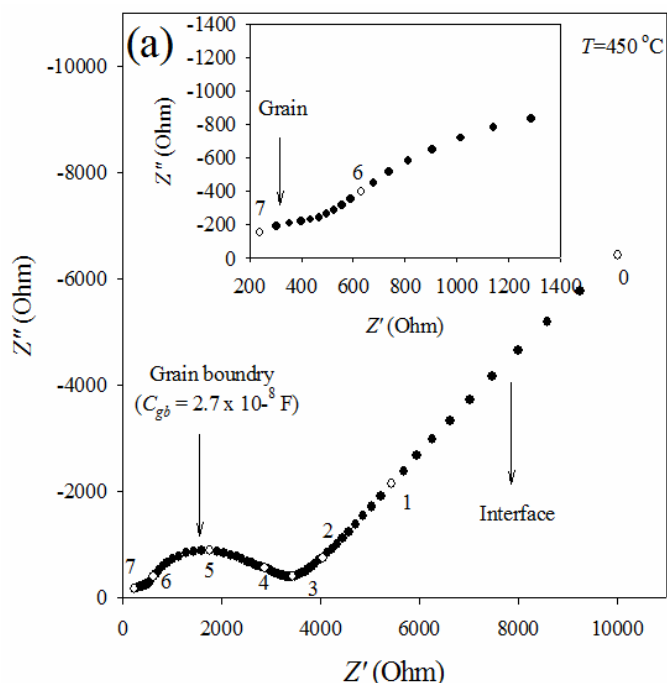


Figure 3:(a) XRD spectra for calcined powder at $T=1100\text{ }^{\circ}\text{C}$ for 12 h and 36 h and (b)XRD spectra for BZY10 prepared by different methods

Figure 3 (a) shows XRD spectra for calcined powder at 1100 °C for 12 h and 36 h. It is noticed that, a peak of BaCO₃ still exist even after calcined at $T=1100$ °C for 36 h. However after calcination at $T=1300$ °C for 12 h, a single phase BaZrO₃ was observed. The result confirmed that the sample was single phase with cubic structure (JCPDS card 06-0399) as shown in Figure 3(b). All the peaks can be indexed to Miller indices (110), (110), (111), (200), (210), (211), (220), (310) and (222), respectively. As a comparison, BaZrO₃ that prepared by SSR is also included. The calcination temperature is 200 °C higher than that prepared by Pechini method as shown in Figure 3(b). A compact BaZrO₃ with density ≈ 92 % relative of theoretical density were successfully obtained at sintering temperature 1500 °C for 10 h which is 200 °C lower than reported by Kreuer et al [13]. Possible explanation is that ZnO may react with barium oxides to form some intermediate barium zinc oxides which may have relatively lower melting point therefore decreasing the sintering temperature of BaZrO₃ based perovskite oxides. Another possibility is that zinc entered the perovskite lattice and Zn containing perovskite exhibits a lower melting point. Therefore it is easier to be sintered dense. The ionic size of Zr⁴⁺ and Zn²⁺ ions are 0.72 and 0.74 Å respectively which are fairly close. From this point of view, Zn²⁺ ions are easier to enter the BaZrO₃ lattice than other transition ions and this could be the reason why zinc is more effective additive than other transition metal oxides [6].

Electrical conductivity



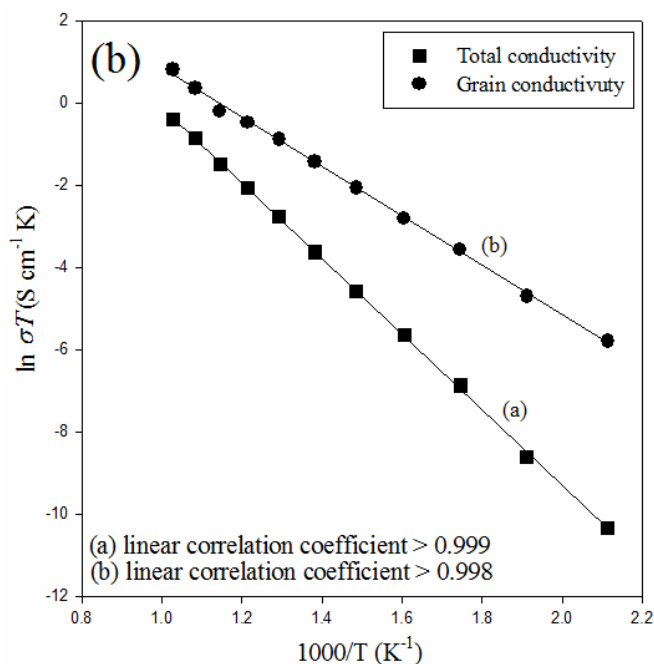


Figure 4:(a) Impedance spectrum of BZY10 at $T=450$ °C (number 0 to 7 is n value for 10^n in the frequency range of impedance measurement and (b) Graph of the total and grain conductivities for BZY10 in water-saturated nitrogen.

Figure 4(a) shows the impedance spectrum at $T= 450$ °C. The spectrum consists of three semi-circles. The small arc at high frequencies is due to grain response, the second arc at intermediate frequency is attributed to the grain boundary response and the third arc at low frequency is corresponding to electrode-electrolyte interface. Detail analysis of impedance spectrum was reported in ref [14]. The grain and total conductivities of the sample in the temperature range 200 to 700 °C obey Arrhenius law as shown in Figure 4(a). The activation energy of the grain (E_{ag}) and total (E_{aT}) of the sample estimated from the graph $\ln \sigma T$ ($S\ cm^{-1}\ K$) versus $1000/T$ (K^{-1}) was found to be 0.52 eV and 0.79 eV, respectively.

CONCLUSION

A $BaZr_{0.95}Zn_{0.05}Y_{0.1}O_{3-\alpha}$ (BZY10) sample was successfully prepared by Pechini method (PM) using metal nitrate-salt after calcination at $T=1300$ °C. SEM results also showed that, the particles size obtained in this work are in nanometer range. The total conductivity of the sample at $T= 700$ °C is 6.9×10^{-4} $S\ cm^{-1}$. Further works to improve the sample preparation are still in progress and will be reported elsewhere.

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