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INFLUENCE MOLAR RATIO OF COMPLEXANT AGENT TO METAL IONS ON THE PARTICLE SIZE OF Y^{3+} DOPED BAZRO$_3$ PREPARED BY PECHINI METHOD

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ABSTRACT

The results reported here based on a study $BaZr_{0.9}Zn_{0.05}Y_{0.1}O_{2.95}$ powders prepared by the Pechini method using metal-nitrate salts as starting materials. Metal nitrates and citric acid were used to prepare the metal-carboxylic acid complexes. The polyesterification with ethylene glycol when the complexes were heated at 100 ºC and will produce a homogenous polymer resin. The different molar ratio of the citric acid to metal ions were prepared, then the powders were studied using Fourier transform infrared (FTIR) spectroscopy and X-ray diffraction (XRD) and field emission scanning electron microscope (FESEM). From XRD results, $BaCO_3$ still exist even after calcination at T = 1100 ºC for 30 h. The particle sizes of powders were observed in range of 20 – 200 nm.

Keywords: *$BaZrO_3$, Pechini method, Citric acid, Polyesterification*

INTRODUCTION

Protons conducting solid electrolytes have got significant attention due to their wide range of technological applications, especially in fuel cells, batteries, gas sensors, hydrogenations/dehydrogenation of hydrocarbons and electrolysers (Iwahara 1995; Norby 1999). $BaCeO_3$-based proton conductors have shown high proton conductivity. However, their chemical stability at the operating conditions is not sufficient, because their easily decomposed into $BaCO_3$,

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$Ba(OH)_2$, and CeO_2 when exposed under CO_2 and H_2O containing atmosphere (Kreuer 1999; Ryu & Haile 1999).

In contrast to the alkaline-earth cerate-based proton conductors, alkaline-earth zirconate-based conductors show sufficient chemical stability at the operating conditions. Especially, $BaZrO_3$-based proton conductors have attracted many researchers, because it shows high proton conductivity next to $BaCeO_3$ based proton conductors (Bohn & Schober 2000; Schober & Bohn 2000; Slade et al. 1995). Yttrium has been selected as the dopant because Y^{3+} doped $BaZrO_3$ shows high proton conductivity among other dopant (Iwahara et al.1993). The commonly used method is solid state reaction (SSR) which needs high calcination and sintering temperatures. A dense $BaZrO_3$ ceramic was achieved by sintering at very high temperature e.g 1700 ºC (Azad & Subramaniam 2002; Bohn & Schober 2000). To overcome the problem of SSR, a wet chemical method (WCM) was used in this study. It has been proven that WCM can produce powders with high purity, high degree of crystallinity, and homogenous fine powder at temperature lower than that used in SSR.

It has been reported that solid powders yttria stabilized zirconia (YSZ) were successfully prepared by the modified Pechini method (Robert et al. 2003), in which citric acid and ethylene glycol are polymerized around metal ions. Metal nitrates salts ware used as precursors because metal nitrates have more favorable decomposition kinetics compared to the carbonate (Azad & Subramaniam 2002), acetate and chloride bases (Osman et al. 2006).

The Pechini method (Pechini 1967) is an alternative to the convectional sol gel method. In this method, the chelates are formed between metal ions and a α-hydroxcarboxylic acid acting as a chelating agent. Later, ethylene glycol (EG) is added as a solvent for the process of polymerization between citric acid and ethylene glycol. The chelate complexes undergo polyesterification when heated in the presence of ethylene glycol and form a homogenous resin. Because of homogenous starting solution, this technique leads to closer combination of mixed oxides, which may enhance strong interaction between metals ion. The Pechini method has been used as an alternative method to obtain ceramic materials for different applications due to its several advantages such as low temperature process, low cost and simplicity. Ethylene glycol greatly inhibits metal ions segregation and achieves a homogenous precursor in the polymerization of citric acid-metal complexes. The amount of citric acid used as a chelating ligand plays an important role in keeping the homogeneity of precursor.

EXPERIMENTAL

$Ba(NO_3)_2$ (R&M Chemicals, 99.0% purity), $Y(NO_3)_3$ $6H_2O$ (Aldrich, 99.9%), $Zn(NO_3)_2$ $6H_2O$ (Fluka, 99.0%), and $ZrO(NO_3)_2$ xH_2O (Acros Organics, 99.5%), x = 4.8385, as determined by thermo gravimetric analysis (TGA), were used as starting materials. The initial molar ratio of citric acid, ethylene glycol to total metal ions is 3:1:1 for S1 and 1:3:1 for S2. A detail procedure in obtaining sol and gel was reported in Osman et al. (2009). The gel then was heated at temperature 120 − 260 ºC 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= 500 ºC for 10 h and at T = 800 ºC for 10 h. The powders obtained from the pre-calcination process were calcined at 1100 ºC for 30 h. The calcined powders were pressed to into pellets (13 mm in diameter) which were sintered at 1350 ºC for 6 hours.

The characterization of the IR vibration bands in BZY10 was carried out in the range of 4000 cm^{-1} – 400 cm^{-1} using Fourier Transform Infra Red (FTIR) analyzer model Nicolet 380 (Thermo Electron Corporation). Phase identification of the calcined powder was determined using X-ray diffraction (XRD) Bruker D8 advance (Cu-Kα;λ = 1.5418 Å from 20º to 80º in steps of 0.025 º and its morphology of the calcined powder was observed using FESEM model Supra 55 VP.

RESULTS AND DISCUSSION

Fourier transforms infrared (FTIR) spectroscopy

Figure 1 shows the FTIR spectra of powders prepared from different molar ratios of citric acid to metal cations after calcination at 1100 ºC for 30 h. A broad absorption band around 3670 cm^{-1} appeared in the IR spectra are the characteristic of absorbed water or hydroxyl group in alcohol. The twin peaks around 2350 cm^{-1} are attributed to the artefact from instrument (Nafisah. 2009). Additionally, the absorption bands at 1420 cm^{-1} and 850 cm^{-1} reveal the existence of carbonate (CO_3^{2-}) (Boshini et al. 2003). The carbonates probably are influenced by the incomplete combustion of the excessive organic matters while calcination. From the FTIR results, it seems that calcination at temperature higher than 1100 ºC is needed to successfully eliminate the carbonate materials. The large vibration observed around 530 cm^{-1} in the calcined powder is due to Zr-O vibration in the perovskite structure.

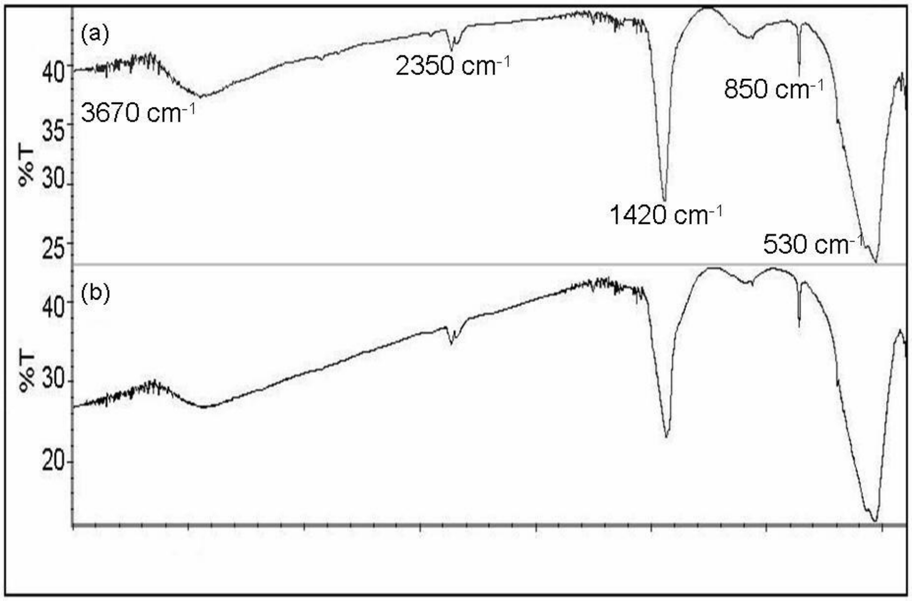

Figure 1: FTIR spectra of BZY10 powder prepared from various molar ratio of CA/EG to metal ions and calcined at 1100 ºC for 30 h. Molar ratio of CA/EG to metal ions at: (a) 3:1:1 and (b) 1:3:1.

X-Ray Diffraction (XRD)

Figure 2 shows XRD spectra for the powders calcination at 1100 ºC for 30 h with different molar ratio of citric acid to metal cations. All the existing peaks are matched to those of $BaZrO_3$ as in JCPDS card no. 06-0399. All the peaks can be indexed to Miller indices (100), (110), (111), (200), (210), (211), (220), (310), and (222), respectively. After calcination at 1100 ºC for 30 h $BaCO_3$ still exist and this agrees with the FTIR results. As seen from the XRD spectra, the peak of $BaCO_3$ is decrease when molar ratio of citric acid to ethylene glycol is lower than high molar ratio citric acid to ethylene glycol. According to the XRD results, the peak due to perovskite phase is getting stronger and sharper as the molar ratio of citric acid decreases, indicating that an increases in the degree of long-range order in the perovskite lattice. Combining the XRD results with FTIR spectra a perovskite structure accompanied with carbonate phase is observed as shown in Figure

2, which is in accordance with the FTIR results discussed. It indicate that at this calcination temperature there is still unreacted carbonated existed.

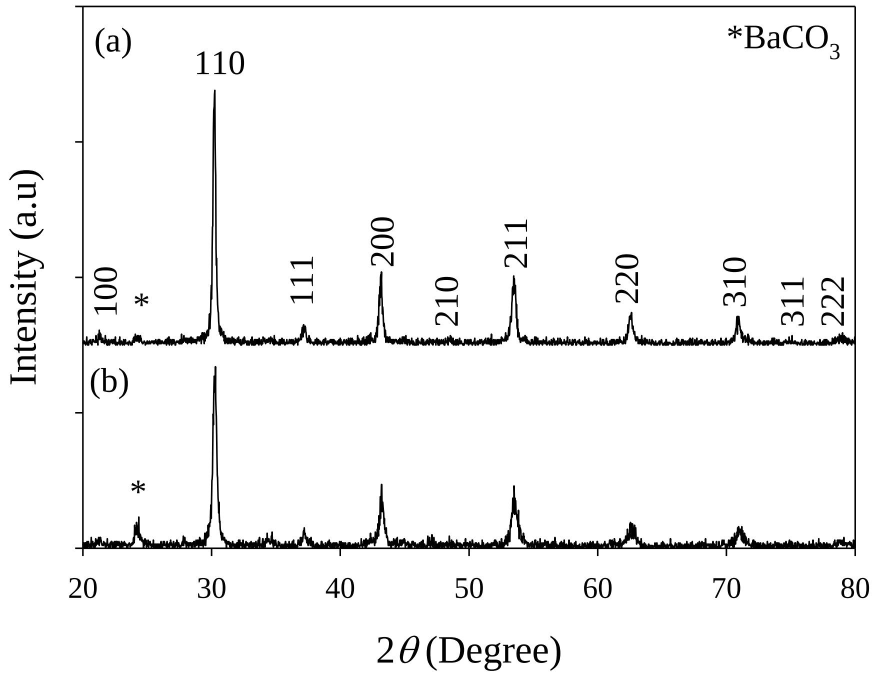

Figure 2: XRD spectra of BZY10 powders prepared from various molar ratio of CA/EG to metal ions and calcined at 1100 ºC for 30 h. Molar ratio of CA/EG to metal ions at: (a) 3:1:1 and (b) 1:3:1.

Scanning Electron Microscopy (SEM)

Figure 3 shows the FESEM micrographs of BZY10 sample powders with different molar ratio of complexant agent calcination at 1100 ºC for 30 h. For the S1 sample, the particles size in the range 20-120 nm. For S2, the particle sizes in the range 90-200 nm. It can be explained that the higher molar ratio of citric acid to ethylene glycol, the particles are smaller and tend form of large and hard agglomerates. It is caused by the higher ratio of COOH (carbonyl acid group) reacted with hydroxyl from ethylene glycol (Yang et al. 2005). Lessing (1989) has concluded that it would be impossible to obtain unagglomerated powder through calcination of a dense and rigid polymer precursor.

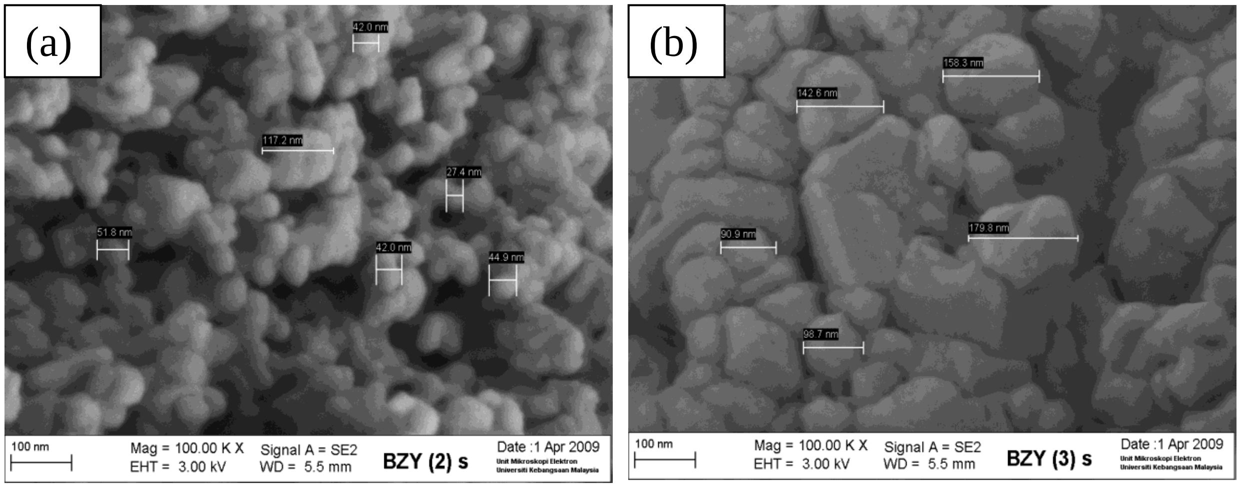

Figure 3: SEM image of BZY10 powders prepared from various molar ratio of CA/EG to metal ions and calcined at 1100 ºC for 30 h. Molar ratio of CA/EG to metal ions at: (a) 3:1:1 and (b) 1:3:1.

The particle sizes obtained in this work were smaller than that reported by Azad & Subramaniam (2002) for $BaZrO_3$. The average particle size distribution for their sample, prepared by solid state reaction based on nitrate was about 0-1 and 2-7 µm at calcination temperature 1000 ºC for 4 h. For Figures 3 (a), the particle sizes of powders after calcination at 1100 ºC for 30 h, in range 20 − 120 nm. Due to the agglomeration effect, which increases with calcination temperature, with larger of agglomerates, the powder packing reduces and increases the volume of the sample (Azad & Subramaniam 2002). For Figures 3 (b), the particle sizes in range 90-200 nm. These large particle sizes also merge with each other to form continuous shape plate. Thus, the pellet for the sample with molar ratio of citric acid/ethylene glycol is 3:1 is crack while the pellet for the sample with molar ratio of citric acid/ethylene glycol is 1:3 is ≈ 95 % relative of theoretical density.

CONCLUSION

$BaZr_{0.9}Zn_{0.05}Y_{0.1}O_{2.95}$ powders were prepared by Pechini method with different molar ratio of citric acid to metal ions is 3:1 and 1:1. Precursor based nitrate-salts were dissolved in deionized water with citric acid, ethylene glycol were used to produce the resin of chelate from polyesterification between citric acid and ethylene glycol. The resulting effect on the powders properties were studied using FTIR, XRD and FESEM. From FTIR and XRD results, shows that the lower molar ratio of citric acid to metal ions which is 1:1, give the lower carbonate phase in perovskite structure. But for the particle sizes as shown, indicate that the lower molar ratio to metal ions give large particle sizes which is in range 90 − 200 nm then the higher molar ratio of citric acid to metal ions are 20 − 120 nm.

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