*Solid State Science and Technology, Vol. 69, No 2 (2010) 36-44*
ISSN 0128-7389

# THE EFFECT OF DIFFERENT MOLAR RATIO CITRIC ACID AND ETHYLENE GLYCOL TO METAL CATION ON THE CERAMICS POWDER OF $Y^{3+}$ DOPED BAZRO$_3$

Siti Noraini Abu Bakar[1], Ibrahim Abu Talib[1] and Nafisah Osman[2]

[1] *Faculty of Science and Technology, UKM, 43600 Bangi, Selangor, Malaysia*

[2] *Faculty of Applied Science, UiTM, 02600 Arau, Perlis, Malaysia*

## ABSTRACT

Sample of $BaZr_{0.85}Zn_{0.05}Y_{0.1}O_{2.95}$ (BZY10) compound were prepared by the Pechini method with different molar ratios of citric acid and ethylene glycol to metal ions using metal nitrate-salts. Metal organic complexes were obtained from the polymerization process between metal nitrate, citric acid and ethylene glycol. After heated at 120 °C, a clear viscous solution or polymer resin containing metal in solid solution was formed. The resin was annealed at 3 different temperatures to remove the organic materials and produce the desired oxide powder. The powder was characterized by a Fourier Transform Infrared (FTIR), X-ray Diffractometer (XRD) and Field Emission Scanning Electron Microscope (FESEM). FTIR and XRD results showed that $BaCO_3$ still exist even after calcined at T= 1100 ºC for 30h. The loose particles size for BZY10 powders obtained from FESEM and particle size analyzer was in the range 20−100 nm.

## INTRODUCTION

Protons conducting solid electrolytes have got significant attention due to their wide range of technological applications, especially in solid state ionics devices [1].Alkaline-earth zirconate-based conductors such as $BaZrO_3$ show enhance chemical stability and high proton conductivity compare to cerate-based conductors [2-3]. Recently, in terms of sample preparation, the compounds have been widely prepared by wet chemical methods (WCMs) in order to overcome the drawback of solid state reaction (SSR) method [4]. 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 [5]. The principle of the Pechini process is based on the ability of carboxylic acids to chelate the metal ions, which can undergo polyesterification with polyhydroxyl alcohols. 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. 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

Corresponding Author: noraini.abubakar@gmail.com

chelating ligand plays an important role in keeping the homogeneity of precursor.

It has been reported that solid powders of yttria stabilized zirconia (YSZ) were successfully prepared by the modified Pechini method [6], in which citric acid and ethylene glycol are polymerized around metal ions. Metal nitrates salts ware used in this study as precursors because metal nitrates have more favorable decomposition kinetics compared to the carbonate [7], acetate and chloride bases [8].

## METHODOLOGY

The BZY10 was synthesized by the Pechini method using the following precursors: $Ba(NO_3)_2$ (R&M Chemicals, 99.0% purity), $Y(NO_3)_3$ $6H_2O$ (Aldrich, 99.9% purity), $Zn(NO_3)_2$ $6H_2O$ (Fluka, 99.0% purity), and $ZrO(NO_3)_2$ $xH_2O$ (Acros Organics, 99.5% purity), where $x = 4.8385$. The different molar ratios of citric acid (CA) and ethylene glycol (EG) to metal cation were prepared as presented in Table 1. A detail procedure in obtaining sol and gel was reported in Osman et al. [9]. The gel was heated at temperature of 120 − 260 ºC until it became a dark brown viscous gel. The viscous gel was dried at 300 ºC overnight and then further heated at T= 500 ºC for 10h and 1100 ºC for 30h. The IR vibration bands of carbonate species in S1 to S5 were determined using a Fourier Transform Infra Red (FTIR) analyzer model Nicolet 380 (Thermo Electron Corporation). Phase identification of the calcined powder was determined using a X-ray diffractometer (XRD) Bruker D8 Advanced (Cu-Kα;$\lambda = 1.5418$ Å) from 20º to 80º in steps of 0.025 º. Particle size measurements for the calcined powder were performed using the laser scattering particle size distribution analyzer model Malvern Nano S (ZEN 1600). Morphology of the calcined powder was observed using a field emission scanning electron microscope (FESEM) model Supra 55 VP.

Table 1: Nomenclature for the sample BZY10 with different molar ratio of citric acid and ethylene glycol to metal ions

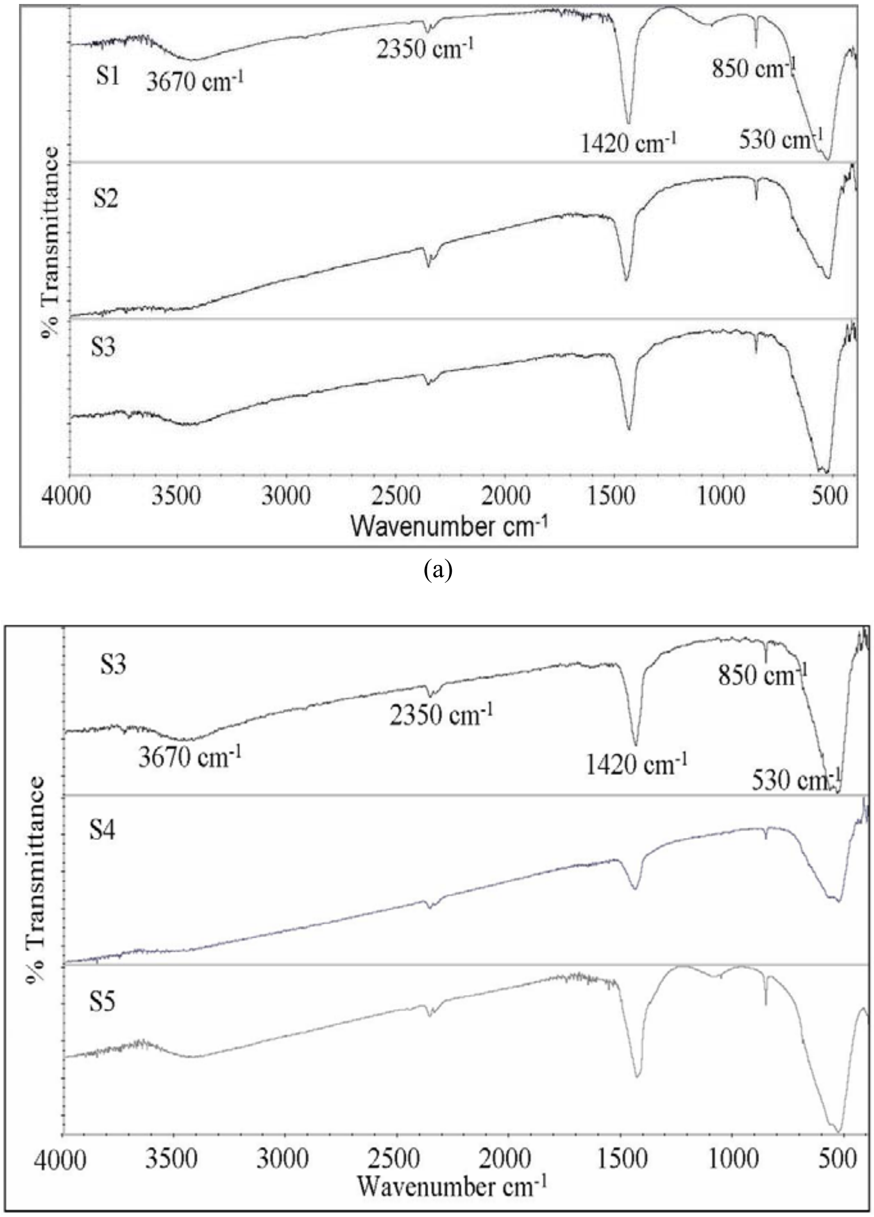
| Samples | Citric Acid | Ethylene Glycol | Metal cations |
|---|---|---|---|
| S1 | 3 | 1 | 1 |
| S2 | 2 | 1 | 1 |
| S3 | 1 | 1 | 1 |
| S4 | 1 | 2 | 1 |
| S5 | 1 | 3 | 1 |

## RESULTS AND DISCUSSION

Figure 1 shows the FTIR spectra for S1 to S5 after the powders were calcined at 1100 ºC for 30 h. A broad absorption band around 3670 $cm^{-1}$ is due the absorbed water or hydroxyl group in alcohol. A twin peaks around 2350 $cm^{-1}$ are attributed to the artefact from instrument [10]. The existing of absorption bands at 1420 $cm^{-1}$ and 850 $cm^{-1}$ indicates that the carbonate ion ($CO_3^{2-}$) species still remained insight the sample [11]. The presence of carbonates ion residue might be due to the incomplete combustion of

Corresponding Author: noraini.abubakar@gmail.com

the excessive organic matters during heat treatment. The large vibration band around 530 cm$^{-1}$ is due to Zr-O vibration in the perovskite structure. S2 and S4 show a reduced amount of carbonate species than S1, S2 and S5. It can be explained that the molar ratio of citric acid and ethylene glycol that should be used to ease the carbonate species is 2 molar respectively.

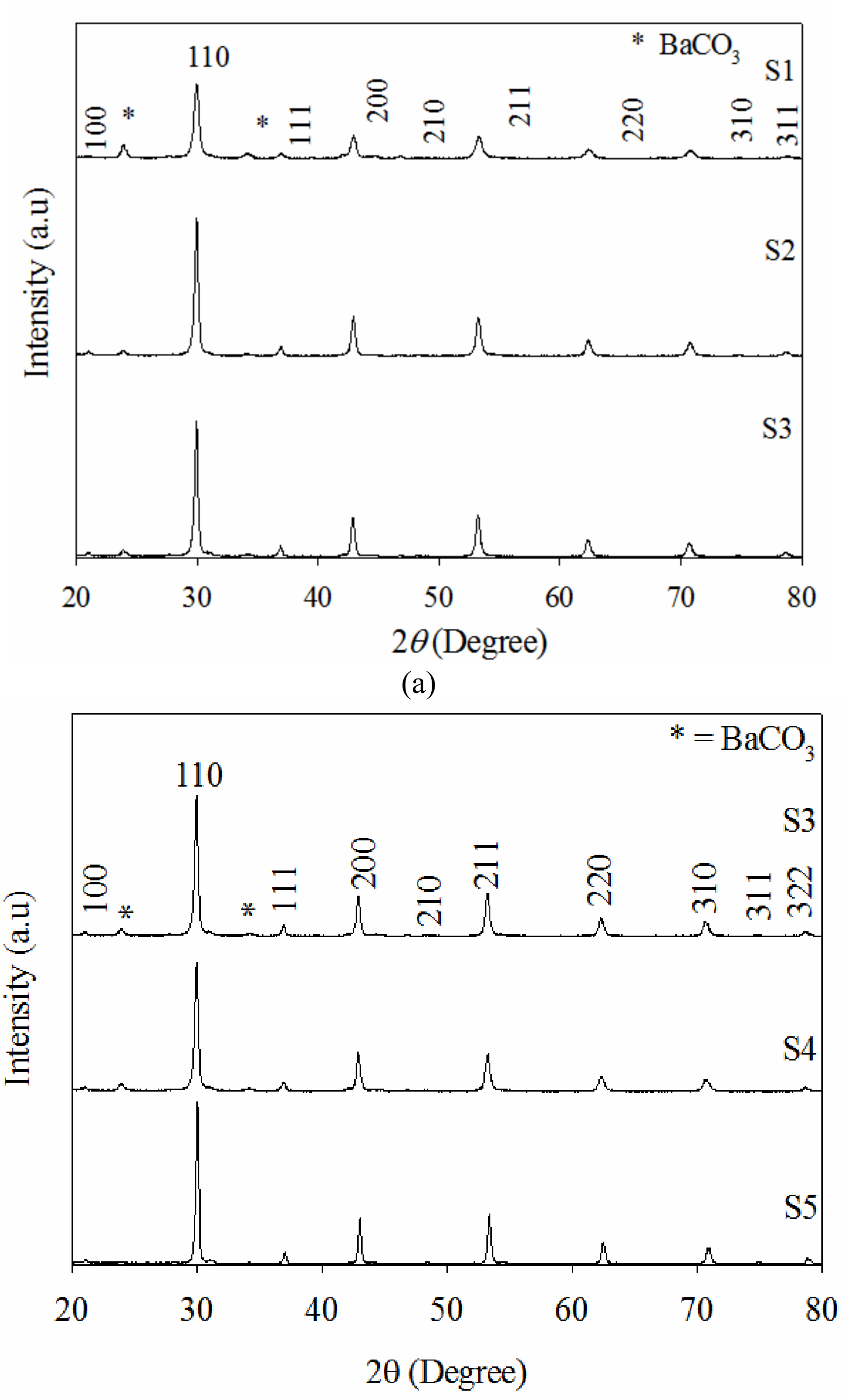


(a)

(b)

Figure 1: FTIR spectra of BZY10 powders prepared from different molar ratio of CA to metal ions and EG to metal ions (a) Molar ratio of CA to metal ions at: (S1) 3:1:1, (S2) 2:1:1 and (S3) 1:1:1 (b) Molar ratio of EG to metal ions at: (S3) 1:1:1, (S4) 1:2:1 and (S5) 1:3:1 after calcination at 1100 ºC for 30h.

Corresponding Author: noraini.abubakar@gmail.com

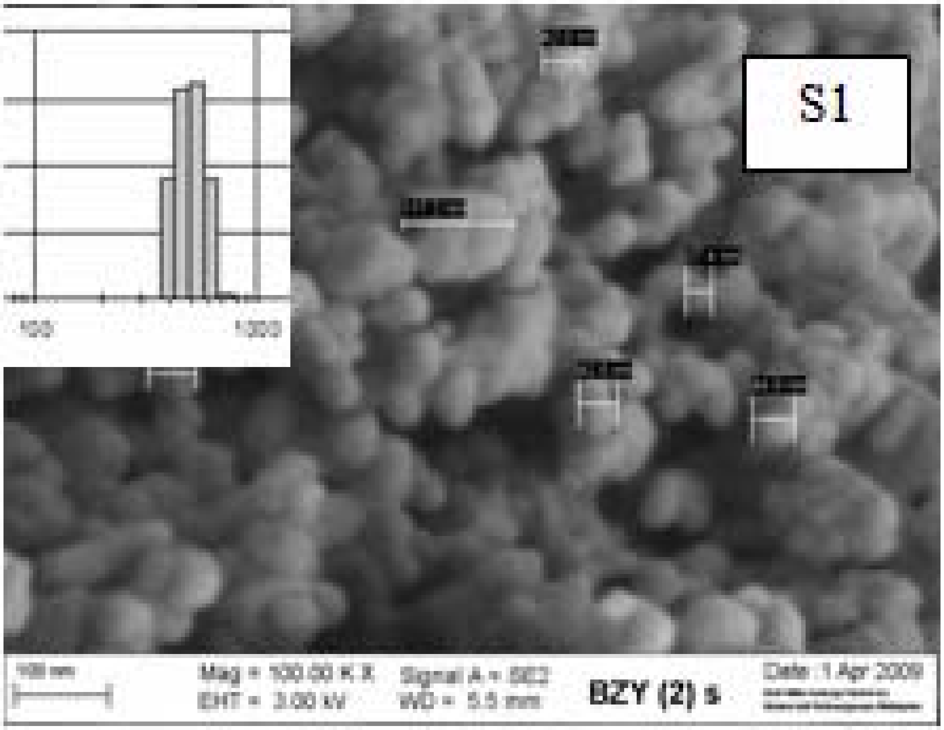


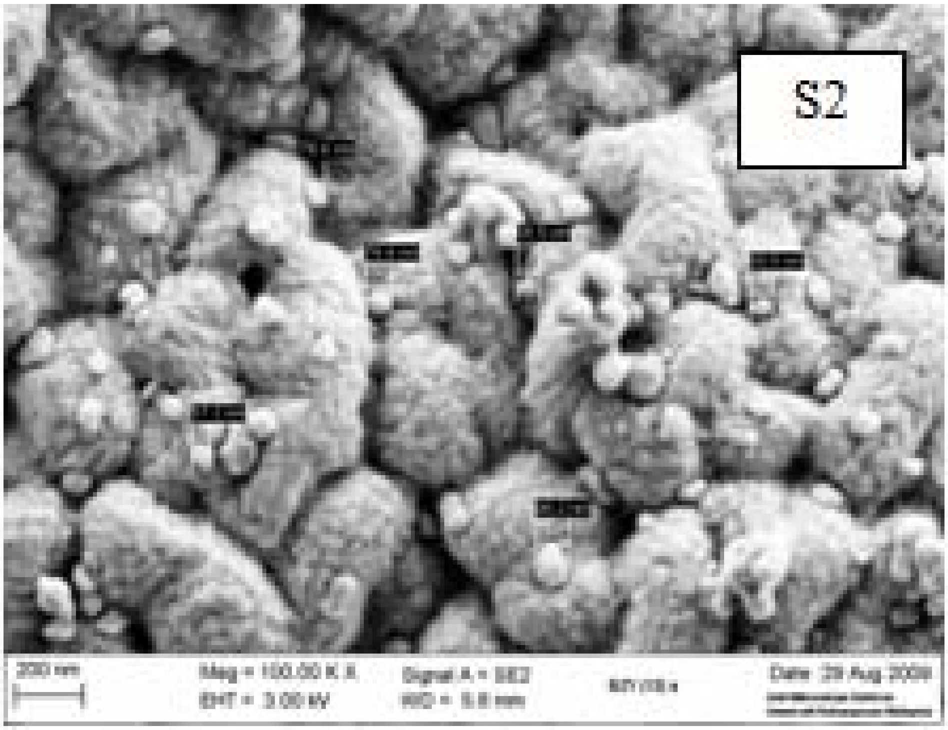
(a)

(b)

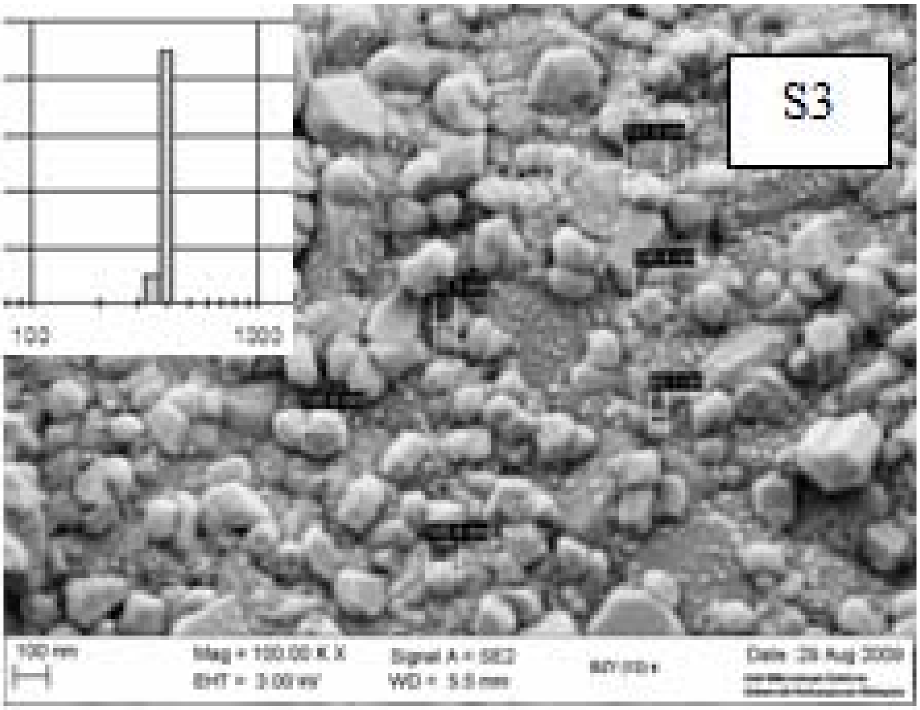
Figure 2: XRD spectra of BZY10 powders prepared from different molar ratio of CA to metal ions and EG to metal ions (a) Molar ratio of CA to metal ions at: (S1) 3:1:1, (S2) 2:1:1 and (S3) 1:1:1 (b) Molar ratio of EG to metal ions at: (S3) 1:1:1, (S4) 1:2:1 and (S5) 1:3:1 after calcined at 1100 ºC for 30 h

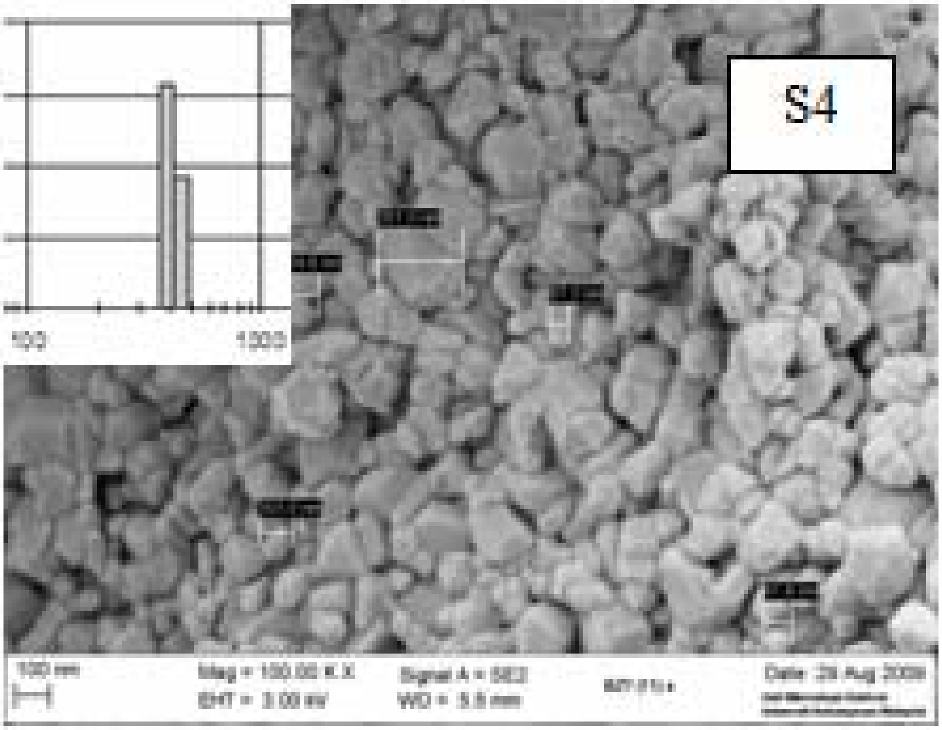
Corresponding Author: noraini.abubakar@gmail.com





Corresponding Author: noraini.abubakar@gmail.com


S3
100
1000
100 nm
Mag = 100.00 K X
EHT = 3.00 kV
Signal A = SE2
WD = 5.5 mm
Date :28 Aug 2009


S4
100
1000
100 nm
Mag = 100.00 K X
EHT = 3.00 kV
Signal A = SE2
WD = 5.5 mm
Date :28 Aug 2009

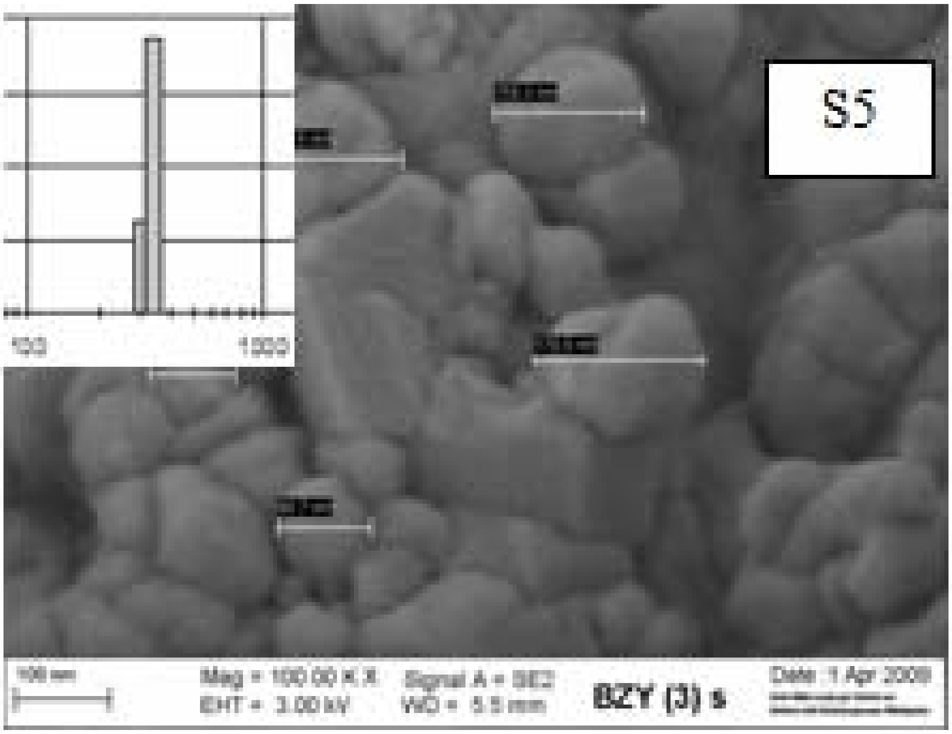


Figure 3: FESEM images of BZY10 powders prepared using different molar ratio of CA and EG to metal ions. Molar ratio of CA: EG: metal ions at: (S1) 3:1:1, (S2) 2:1:1, (S3) 1:1:1, (S4) 1:2:1 and (S5) 1:3:1

Figure 2 shows XRD spectra for S1, to S5 after the samples were calcined at 1100 ºC for 30 h. All the peaks are matched to $BaZrO_3$ (JCPDS card no. 06-0399) except for the small peaks at $2\theta \approx 23.9^{o}$ and $34.1^{o}$ that are due to the remaining carbonate species as also been observed in the FTIR analysis. Figure 2(a) shows the peak due to perovskite phase is getting intense 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. While Figure 2(a) shows the characteristic diffraction peaks appear in the same position and the diffraction peaks have almost the same intensity. It can be concluded that the amount of ethylene glycol has no effect on the phase of the product [12].

Figure 3 and Table 2 show the FESEM micrographs and particle size of the loose particle and agglomerate for the samples S1 to S5, respectively. Figure 3 shows the particles are spherical in shape and have sizes in range 20-100 nm whereas diameters for the agglomerates are 100-300 nm. S1 has smaller particles size than others but tends to form agglomerates. It can be explained that at higher molar ratio of citric acid to metal ions the COOH (carbonyl acid group) reacted with hydroxyl from ethylene glycol to form large and hard agglomerates [13]. On the other hand, S5 has larger particles and less agglomerates. These results also inline with the particle distribution as insert in Figure 3. The loose particles for all samples cannot be measured by the particle analyzer due to agglomerates effect as reported by Taglieri et al. [14] and Osman et al. [9].

Corresponding Author: noraini.abubakar@gmail.com

Table 2: Particle size of the loose powders and agglomerates for the BZY10 sample obtained from FESEM and particle size analyzer

| Sample | Loose powders (nm) | | Agglomerates (nm) | |
|---|---|---|---|---|
| | FESEM | Particle Analyzer | FESEM | Particle Analyzer |
| S1 | 10 – 60 | – | 70 – 200 | 300 – 800 |
| S2 | 40 – 100 | – | 100 – 200 | 400 – 500 |
| S3 | 50 – 100 | – | 100 – 300 | 300 – 450 |
| S4 | 50 – 100 | – | 100 – 300 | 300 – 500 |
| S5 | 80 – 100 | – | 100 – 200 | 300 – 400 |

## CONCLUSION

$BaZr_{0.95}Zn_{0.05}Y_{0.1}O_{3-\alpha}$ (BZY10) samples were successfully prepared by Pechini method (PM) using metal nitrate-salts. The samples were prepared with different molar ratio of citric acid and ethylene glycol to metal ions. FTIR showed that 2 molar of citric acid and ethylene glycol were the optimum molar ratio to reduce carbonate species. XRD results showed that by decreasing the molar ratio of citric acid the reflective peaks in the prepared compound became more intense and sharper. In contrast, with higher molar ratio of ethylene glycol the peaks have almost the same intensity. FESEM micrographs showed that by increasing the molar ratio of citric acid to metal ions, the particle size became gradually smaller and tend to form agglomerates. However, when the molar ratio of ethylene glycol to metal ions increased, the particle became slowly larger and less agglomerate presence. The expectation to get nanopowders with less percentage of agglomerates for the ceramic powders of BZY10 is not successfully achieved in this work. Therefore, the extension works are under progress and will be reported elsewhere

## ACKNOWLEDGMENT

The authors would like to thank the Minister of Higher Education for the Grant UKM-ST-01-FRGS0056-2006.

## REFERENCES

[1] H. Iwahara, (1995) "*Technology Challenges in the Application of Proton Conducting Ceramics" Solid State Ionics*, **77** 289-298,

[2] H.G. Bohn, & T. Schober, (2000). *Electrical Conductivity of the High-Temperature Proton Conductor* $BaZr_{0.9}Y_{0.1}O_{2.95}$. *Journal of the American Ceramic Society* **83** 768-772

[3] R.C.T. Slade, S.D. Flint, & N. Singh, (1995). *Investigation of Protonic Conduction in Yb- and Y-Doped Barium Zirconates. Solid State Ionics* **82** 135-141

[4] S.M. Haile & P. Babilo, (2005). *Enhanced sintering of yttrium-doped barium*

Corresponding Author: noraini.abubakar@gmail.com

*zirconate by addition of ZnO. Journal American Ceramic Society* **88** 2362−2368

[5] M.P. Pechini, U.S. Patent **3** (1967). *Method of Preparing Lead and Alkaline Earth Titanates and Niobates and Coating Method Using the Same to Form a Capasitor* 330-697.

[6] C.L. Robert, F. Ansart, C. Deloget, M. Gaudon, A. Rousset, (2003) *Dense Yttria Stabilized Zirconia: Sintering and Microstructure. Ceramic International* **29** 151-158

[7] A.M. Azad. & S. Subramaniam, (2002). *Synthesis of $BaZrO_3$ by a Solid State Reaction Technique Using Nitrate Precusors. Materials Research Bulletin* **37** 85-97

[8] N. Osman, A.M. Jani, I.B. Talib, (2006). *Synthesis of Yb-doped $Ba(Ce,Zr)O_3$ Ceramic Powders by Sol-gel Method. Ionics* **12** 379-384

[9] N.Osman, I.A. Talib & H. A. Hamid, (2009). *Effect of stoichiometric composition and diferent metal salts on the phase formation of cerate-zirconate ceramics. Sains Malaysiana* **38 (3)** 401-405.

[10] N. Osman, Tesis PhD. Universiti Kebangsaan Malaysia (2009) *Pencirian bahan elektrolit pepejal berasaskan $Ba(Ce,Zr)O_3$ yang didopkan dengan $Yb^{3+}$ sebagai konduktor proton pada suhu pertengahan, ($400 \leq T$ ºC $\leq 750$).*

[11] F. Boschini, B. Robertz, A. Rulmont & R. Cloots, (2003). *Preparation of nanosized barium zirconate powder by thermal decomposition of urea in an aqueous solution containing barium and zirconium, and by calcination of the precipatate. Journal European Ceramics Society* **23** 3035−3042

[12] Chen Weifan, Li Fengsheng, Liu Leili & Li Yongxiu, (2006). *Synthesis of nano-sized yttria via a sol gel process based on hydrated yttrium nitrate and ethylene glycol and its catalytic performnace for themal decomposition of $NH_4ClO_4$. Journal of Rear Earth.* **24** 543 – 548

[13] W.D. Yang, Y.H. Chang, & S.H. Huang, (2005). *Influence of molar ratio of citric acid to metal ions preparations of $La_{0.67}Sr_{0.33}MnO_3$ materials via polymerizable complex process. Journal of the European Ceramic Society* **25** 3611−3618

[14] G. Taglieri, M. Tersigni, P.L. Villa, and C. Mondelli, (1999). *Synthesis by citrate route and characterization of $BaZrO_3$, a high tech ceramic oxide: preliminary results. International Journal of Inorganic Material* **1** 103-110

Corresponding Author: noraini.abubakar@gmail.com