

Morphology and Elemental Composition of Cerate-Zirconate Compound as-Prepared by a Sol-Gel Technique

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Powder of $\text{BaCe}_{0.54}\text{Zr}_{0.36}\text{Y}_{0.1}\text{O}_{2.95}$ (BCZY) ceramics compound was synthesized by a modified sol-gel method using triethylenetetraamine, TETA as a chelating agent. The samples were dried and calcined at 325 °C and 1100 °C, respectively. The resulting powder properties were characterized using Particle Size Analyzer (PSA), Scanning Electron Microscope (SEM), X-Ray Fluorescence Spectroscopy (XRF) and Energy Dispersive X-Ray (EDX). At calcination temperature of 1100 °C, the sample shows particles with high purity, spherical shape and a single particle size distribution in the range of 342–396 nm. XRF and EDX analysis revealed that the elemental composition of Ba, Ce, Zr and Y present in the sample is almost the same as the nominal stoichiometric composition of BCZY compound. Thus, TETA is one of the potential chelating agents that can be used to synthesize high purity and homogeneous spherically grained cerate-zirconate powders.

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Introduction

Ceramics compound of $\text{Ba}(\text{Ce,Zr})\text{O}_3$ have potential applications as a solid electrolyte in electrochemical devices such as solid oxide fuel cells (SOFC) [1, 2]. Conventional methods used to prepare this ceramics led to high calcination and sintering temperatures [3]. Extensive studies on soft chemistry methods that have the ability to reduce calcination temperature had gain much more interest from researchers world-wide. These chemistry methods have been developed to synthesize submicron-sized to nano-sized oxide powder with excellent properties [4, 5]. The use of relatively low calcination temperature also inhibits the loss of some easily evaporated elements such as Ba. According to Snijkers et al. [3], high firing temperature will create barium deficiency in $\text{Ba}_x\text{Hf}_{0.9}\text{Y}_{0.1}\text{O}_{3-\alpha}$ due to the loss of BaO . Therefore, the main focus of the present work is to synthesize and characterize the BCZY powder as-prepared by one of the soft chemistry method which is a sol-gel technique assisted by TETA and ethylene glycol as chelating agent and polymerization agent, respectively.

2. Experimental details

2.1 Materials

A compound of $\text{BaCe}_{0.54}\text{Zr}_{0.36}\text{Y}_{0.1}\text{O}_{2.95}$ (BCZY) was synthesized by a sol-gel method using metal nitrate salts as starting materials. Triethylenetetraamine, TETA (60%, ACROS) was used as chelating agent and ethylene

glycol, EG (99.96%, ACROS) was used as polymerization agent. The molar ratio of TETA to EG and metal cation was fixed at 3:2:3, respectively.

2.2 Procedure method

A stoichiometric amount of $\text{Ba}(\text{NO}_3)_2$ (99%, ACROS), $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (99.5%, ACROS), $\text{Zr}(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$ (99.5%, ACROS) and $\text{Y}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ (99.9%, Aldrich) was dissolved in de-ionised water and continuously stirred on a hot-plate to make a transparent nitrate solution. TETA was added into the solution followed by ethylene glycol under continuous stirring. A concentrated ammonia solution was added until pH 11. The resulting solution was slowly evaporated on a hot plate at 120 °C. The heating and stirring process was controlled accordingly. During the process, the browning gas (known as NO_x) was released and a dark brown porous gel obtained. The gel was dried at 325 °C in a furnace and yielded yellow fine flakes. The sample was calcined at 1100 °C with heating rate of 10 °C min^{-1} for 10 h to yield light-yellow powder.

2.3 Characterization

The particle size measurement was carried out using laser scattering particle size distribution analyzer model Malvern Nano S-ZEN 1600. Morphology of the particle was observed using a scanning electron microscope (SEM) model Carl Zeiss SMT Supra 40VP. The XRF measurement was carried out to determine the chemical composition of the obtained BCZY powders, using PANalyticalsMiniPal 4 benchtop X-ray fluorescence spectrometer. An Oxford Inca X-Act Electron Dispersive Spectrometer (EDS) attached to the SEM was used to analyze the elemental composition of the calcined powder.

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3. Results and discussion

3.1 Morphology of BCZY powder

Figure 1 shows particle morphology of the BCZY powder as-calcined at $T = 1100\text{ }^{\circ}\text{C}$ for 10 h. The particles have spherical shape with the size in the range of 300–350 nm.

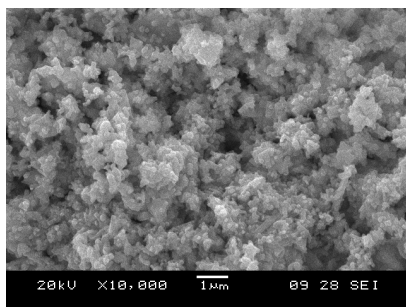


Fig. 1. Secondary electron image of BCZY powder as-calcined at $1100\text{ }^{\circ}\text{C}$ for 10 h.

At high pH value of the solution ($\text{pH} \sim 11$) and at the presence of chelating agent, the sample tends to form spherical particles [6]. These conditions could control the crystal growth in all directions, and therefore led to the formation of rounded particles.

3.2 Particle size distribution

Only one group of particle size distribution in the range of 342–396 nm was observed for as-calcined BCZY powder, which was in the same range with that observed by SEM. The formation of fine particles suggested that the resulting powder consisting of a high inter-dispersion of metal ions and high reactivity of the amorphous precursor [7]. TETA provides a stable metal complexation in the solution, retarding the ions mobility and preserves the atomic scale homogeneity at pH 11 [8]. Subsequently, the use of TETA has retarded the agglomeration of the powder, due to the uniqueness of TETA catalytic effect and high pH value. The role of high pH value is also in-line with the work by Li et al. [9]. They obtained fine NiO-YSZ powders at pH value of 9–13. The addition of the organic ligand, for example the ethylene glycol, also resulted to the reduction of particle size and of the dispersion of the particles.

Elemental composition of BCZY at different sample preparation steps. TABLE I

Elem.	Preparation step				
	Metal nitrate salt	Nitrate salt +TETA +EG	Gel $120\text{ }^{\circ}\text{C}$	Dried powder $325\text{ }^{\circ}\text{C}$	Calcined $1100\text{ }^{\circ}\text{C}$
Ba	1	1	1	1	1
Ce	0.69	0.82	0.72	0.60	0.57
Zr	0.37	0.35	0.34	0.24	0.23
Y	0.11	0.11	0.11	0.07	0.07

3.3 Elemental composition of $\text{Ba}(\text{Ce,Zr})\text{O}_3$

Table I shows the XRF data for elemental analysis of the respective samples, starting with the dilution stage of metal nitrate salts solution and ending with the stage when sample undergoes heat treatment at $1100\text{ }^{\circ}\text{C}$. The percentage composition of each element after being calcined at $1100\text{ }^{\circ}\text{C}$ was almost similar to nominal stoichiometric composition of $\text{BaCe}_{0.54}\text{Zr}_{0.36}\text{Y}_{0.1}\text{O}_{2.95}$. From these results, it was proven that the composition of Ba, Ce, Zr and Y was not deviated from the actual one. The elemental composition analysis of $\text{BaCe}_{0.54}\text{Zr}_{0.36}\text{Y}_{0.1}\text{O}_{2.95}$ at three different areas with the size of $2.5\text{ }\mu\text{m} \times 2.5\text{ }\mu\text{m}$ was also analyzed using EDX analysis and the result is shown in Table II. The obtained ratio of the elements Ba/Ce/Zr/Y was almost similar to the stoichiometric amount of BCZY; B= 1.00, Ce= 0.54, Zr= 0.36, Y= 0.10. However, the ratio of Zr element is high as compared to its nominal stoichiometric ratio. This observation might be due to the fact that $\text{BaCe}_{0.54}\text{Zr}_{0.36}\text{Y}_{0.1}\text{O}_{2.95}$ tends to form Zr-rich phases or Zr-clusters as reported by Osman et al. [10]. TETA coordinates with the metal ions and leads to the homogeneous distribution of ions in gel and the enhancement of the crystallization process results in high purity of BCZY powder.

Elemental composition of BCZY after being calcined at $1100\text{ }^{\circ}\text{C}$. TABLE II

Element	Elemental atomic percentage (%)			
	Area 1	Area 2	Area 3	Average
Y	1.93	1.83	1.67	1.91
Zr	7.53	7.28	7.59	7.47
Ba	16.93	17.17	17.21	17.10
Ce	9.00	8.56	9.47	9.01

4. Conclusions

A cerate-zirconate powder was successfully synthesized using a sol-gel method. The use of TETA and ethylene glycol led to the reduction of calcination temperature that promotes the formation of homogeneous and spherical particles as well as the high purity of samples. This material has been extensively studied as the electrolyte for the proton conducting fuel cells (PCFC) and the results will be reported elsewhere.

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References

- [1] N. Osman, I.A. Talib, H.A. Hamid, *Ionics* **16**, 561 (2010).
- [2] Z. Zhimin, *Solid State Ionics* **178**, 213 (2007).

- [3] F.M.M. Snijkers, A. Buekenhoudt, J.J. Luyten, J. Coymans, M. Mertens, *Scripta Mat.* **51**, 1129 (2004).
- [4] N. Osman, I.A. Talib, H.A. Hamid, *Solid State Sci. and Techn. Lett.* **15**, 62 (2008).
- [5] D. Hennings, H. Schreinemacher, *J. European Ceram. Soc.* **9**, 41 (1991).
- [6] H. Patra, S.K. Rout, S.K. Pratihari, S. Bhattacharya, *Pow. Tec.* **209**, 98 (2001).
- [7] K.A. Singh, L.C. Pathak, S.K. Roy, *Ceram. Int.* **33**, 1463 (2007).
- [8] N.A. Abdullah, N. Osman, S. Hasan, R.M. Nordin, *APCBEE Procedia* **3**, 28 (2012).
- [9] Y. Li, Y.S. Xie, J.H. Gong, Y.F. Chen, Z. T Zhang, *Mater. Sci. and Eng. B* **86**(2), 119 (2001).
- [10] N. Osman, A.M. Jani, I.A. Talib, *Ionics* **12**, 379 (2006).