

A COMPARATIVE STUDY ON BaCe_{0.54}Zr_{0.36}Y_{0.1}O_{2.95} CERAMICS POWDER PREPARED WITH AND WITHOUT SURFACE ACTIVE AGENT

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ABSTRACT

Perovskite-type oxide of BaCe_{0.54}Zr_{0.36}Y_{0.1}O_{2.95} (BCZY) was prepared via a modified sol-gel method using metal nitrate salts as starting material. Citric acid (CA), ethylene glycol (EG) and polyoxyethylene (10) oleyl ether (Brij97) was used as a chelating agent, polymerization agent and surface active agent, respectively. The prepared sample was denoted as S1 (without surfactant) and S2 (Brij97). The resultant powder was characterized by the thermogravimetric analyzer (TGA), X-Ray diffractometer (XRD) and Scanning Electron Microscopy/Electron Dispersive X-Ray (SEM/EDX). TGA result showed that thermal decomposition of the dried powder (T= 325 °C) of S1 was completed at T= 800 °C and S2 at T= 720 °C. At a calcination temperature of 1100 °C, XRD analysis showed that S1 exhibits a mixture of BaCeO₃ and BaZrO₃ impurities, and S2 successfully formed single perovskite phase of Ba(Ce_{0.7}Zr_{0.3})O₃, (JCPDS Card no 089-2485). SEM micrograph revealed that S2 exhibits fewer agglomerates compared to S1. The elemental composition of both samples was not greatly deviated from their nominal stoichiometry.

Keyword: Ba(Ce,Zr)O₃; perovskite-type oxide; surface active agent; modified sol-gel; Brij 97;

INTRODUCTION

Perovskite type-oxides with ABO₃ structure have been found to be an outstanding candidate for the intermediate temperature solid fuel cell (IT-SOFC) electrolyte materials. Typical examples of perovskite-type ceramic oxide are BaCeO₃, SrCeO₃, BaZrO₃, SrZrO₃ and CaZrO₃. Recently, cerate-zirconate ceramic based on perovskite-type oxides for example Ba(Ce,Zr)O₃ have captured most of the researcher's interest due to their excellent properties. According to the previous report, calcination temperature in the range of 1300 °C to 1500 °C is the optimum temperature to obtain single perovskite phase with low impurities of cerate-zirconate ceramic powder [1]. Furthermore, a long firing time and/or multiple calcination steps have been used to

obtain the perovskite-type ceramic oxides. This process is necessary because of the unreacted alkaline earth compounds such as BaO, Ba(OH)₂ and BaCO₃, depending on temperature and atmosphere, destabilize the materials in the presence of CO₂ and H₂O.

To overcome the drawbacks of high temperature treatment, researchers have adopted wet chemical method (WCMs) to produce homogenous particles of perovskite with high crystallinity at relatively low temperature. The sol-gel method is one of the promising synthesis routes and most of the researchers have employed hydrocarboxylic acid (usually citric acid) as a synthesizing aid in promoting small particulate of oxide powders with high purity [2-4]. In this work, nonionic surfactant was used as a catalyst to further improve the morphology and phase formation of a cerate-zirconate ceramic compound.

Surfactants typically play crucial roles in the phase formation and particle size distribution of ceramic powder. Different types of surfactants have different effects on the physico-chemical properties of the obtained powders. Unfortunately, up to date, a systematic comparison of the effects of surfactants on the physico-chemical properties of cerate-zirconate ceramic is rarely reported. In this paper, we report our recent work regarding the synthesizing temperature and morphology of BaCe_{0.54}Zr_{0.36}Y_{0.1}O_{2.95} prepared via a sol-gel route assisted with Brij97 as a surfactant.

METHODOLOGY

Sample Preparation.

High purity of metal nitrate salts of Ba(NO₃)₂ (99%, ACROSS), cerium(III) nitrate hexahydrate, Ce(NO₃)₃·6H₂O (99.5%, ACROS), zirconyl(IV) nitrate hydrate, Zr(NO₃)₂·0.4.8H₂O (99.5%, ACROS), yttrium(III) nitrate hexahydrate and Y(NO₃)₃·6H₂O (99.9%, ACROS) were used as starting materials to synthesize BaCe_{0.54}Zr_{0.36}Y_{0.1}O_{2.95} (denoted as BCZY) ceramic powder. Citric acid monohydrate (99%, Merck), ethylene glycol (99.96%, ACROSS) and polyoxyethylene (10) oleyl ether (Brij97) was used as a chelating agent, polymerization agent and surfactant, respectively.

A stoichiometric amount of each metal nitrate salts was dissolved in 100 ml of deionized water under continuously stirred until transparent solution obtained. CA was added, followed by respective surfactant under continuous stirring. EG was added to aid the polymerization reaction. The pH of the complex solution was maintained at neutral pH value by adding an appropriate amount of ammonium hydroxide solution. The solution was heated on a hotplate with constant stirring and the magnetic stirrer was removed when the solution turns to viscous gel. The resulting gel was further heated until black sponge-like material obtained. On further heating in a furnace at 325 °C for 2 hours, grey fine flakes were obtained. This powder was calcined at T= 1100 °C for 10 hours in a furnace with a heating rate of 10 °C min⁻¹ to yield a light-yellow powder. The prepared samples were labeled as S1 (without surfactant) and S2 (Brij97).

Sample Characterization.

Thermogravimetric analysis (TGA) was done by a PerkinElmer thermogravimetric analyzer (Pyris Diamond). Fifteen milligrams of dried powder was placed in an alumina pan and heated from 25 °C to 1000 °C with a heating rate of 10 °C min⁻¹ under synthetic air (flow rate 100 ml min⁻¹) and the sample's weight change was recorded as a function of temperature. The phase of calcined powders was verified by a Shimadzu X-Ray diffractometer (XRD) using Cu-K_α radiation ($\lambda = 1.5406 \text{ \AA}$) at 2 θ from 20° to 80° in a step of 0.02° and scanning time at 2.5s each step. Morphology of the platinum-coated calcined powders was observed using Nova Nanosem 450 Field Emission Scanning Electron Microscope (FESEM) operating at 5 kV.

RESULTS AND DISCUSSION

Thermal Analysis.

Figure 1 shows the TG thermogram of the dried powders (T= 325 °C). There were three stages of weight loss observed in the both TG signals. The weight loss recorded at each stage was summarized in Table 1. In stage 1, at temperature of $\approx 250 \text{ }^{\circ}\text{C}$, the loss can be attributed for the elimination of water adsorbed at the surface of the sample [5], decomposition of nitrates species and remaining low boiling point organic species [4]. At the temperature of $\approx 650 \text{ }^{\circ}\text{C}$ (stage 2), a significant weight loss was observed can be ascribed to the decomposition of residual oxidizer (nitrates) and the organic compounds such as citric acid and Brij97 in the gel precursor. The appearance of the steep curve in this stage was due to the oxidation and combustion of chelate complexes [6] as well as the burn-out of residual surfactant [7]. The weight loss observed in stage 3 at $\approx 1000 \text{ }^{\circ}\text{C}$ might be originated from the elimination of the trapped carbonate residue that formed as the intermediate products. The beginning of the oxide formation from the intermediate compound also occurred in this stage. It found that the sample with the presence of surfactants (S2) showed the beginning of crystallization process occurred at a lower temperature (T=720 °C) than the sample without surfactant (T= 800 °C). This might due to the presence of a large number of carbon chains in the Brij97 structure which helps to accelerate the decomposition reaction of the sample. There is no further change in the weight loss after stage 3 indicates a complete removal of organic species and decomposition of intermediate products.

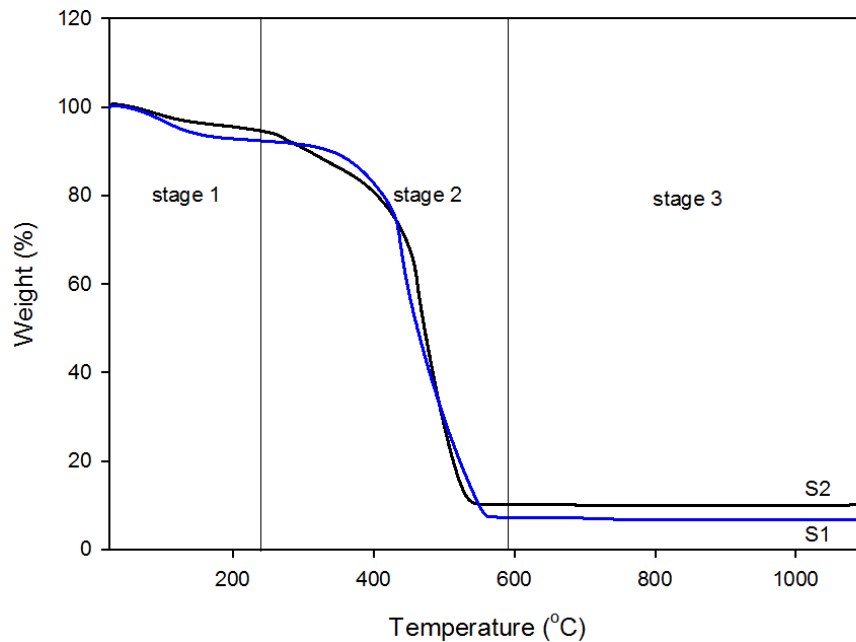


Figure 1: TG profile of the dried powders (T= 325 °C) of S1 and S2

Table 1: Weight loss of the dried powder (T =325 °C) of S1 and S2

Sample	Stage	Temperature range [°C]	Weight loss [%]	Total weight loss [%]
S1	1	27-240	8	93
	2	240-590	83	
	3	590-800	2	
S2	1	27-250	6	92
	2	250-650	85	
	3	650-720	1	

Phase Formation Analysis.

XRD spectra for both calcined samples were shown in the Figure2. The result showed that S2 was successfully formed single perovskite phase of $\text{Ba}(\text{Ce}_{0.7}\text{Zr}_{0.3})\text{O}_3$ (JCPDS card no. 89-2485) after calcined at $T = 1100^\circ\text{C}$. The pronounce peak can be indexed to the index Miller (hkl) of (110), (200), (211), (220) and (310) respectively. The results imply that surfactant (Brij97) was completely removed during the calcination process which is aligned with the TG data (Figure 1). On the other hand, it clearly shows that S1 exhibited incomplete reaction, that consists of two perovskite phases, one presumably barium cerium oxide (BaCeO_3) and the other was barium zirconium oxide (BaZrO_3). The present of these secondary phases was due to the weak ability of citric acid to chelate all the metal cations to form metal complexes resulted in less homogenous distribution of the starting materials. Therefore, high temperature is needed to substitute the Zr^{4+} ion into Ce^{3+} site or vice-versa. In contrast, surfactant exhibits the ability to

adsorb on the surface of the particle and induced the changes in particle surface stoichiometry. This will introduce the inhomogeneities of atomic distribution in the surface layers which could allow the rapid interdiffusion and lattice rearrangement [8] of crystal structure. Hence, the formation of BCZY perovskite phase can be completely formed at lower temperature. Furthermore, micelle might form due to the stability of Brij97 in the aqueous solution resulted in better interaction of CA with metal cations. Thus, more stable metal complexes were formed leading to the formation of BCZY at lower temperature.

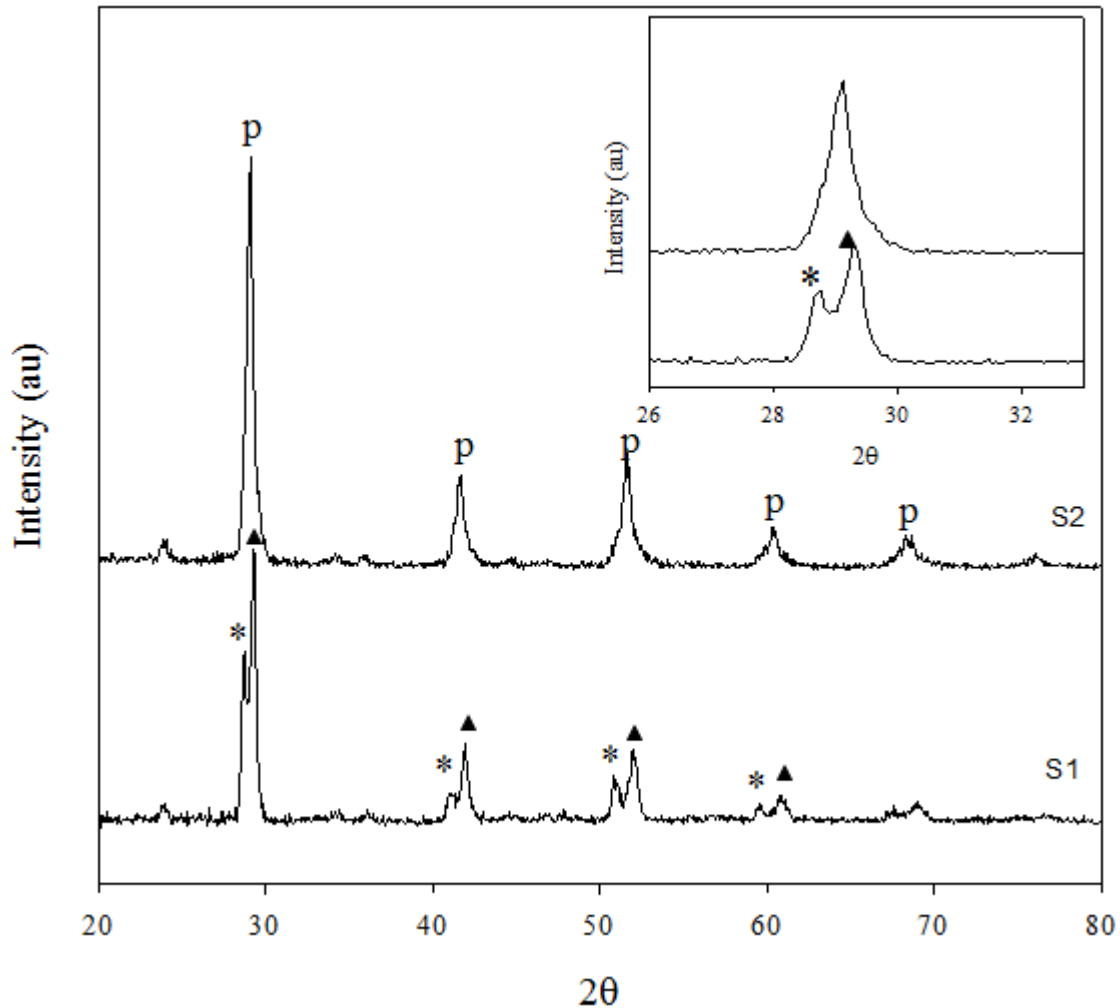


Figure 2: XRD spectra of the calcined samples ($T = 1100\text{ }^{\circ}\text{C}$); *BaCeO₃; ▲ BaZrO₃; p= perovskite

SEM/EDX Analysis.

Figure 3 shows the morphology of the ceramics powder after calcined at $T = 1100\text{ }^{\circ}\text{C}$. S1 exhibits almost spherical in shape with a significant number of agglomerates. The agglomeration of particles was easily formed in the sample without surfactant because of the presence of van der Waals forces and magnetic attraction [9]. However, for S2, the formation of micelle could reduce the intermolecular forces between particles,

resulted in a better dispersion between particles and prevents the aggregation of the final product. The elemental composition of each sample was analyzed using EDX and summarized in Table 2. The results reveal that all the elements were well distributed in the compound after calcined at 1100 °C. The ratio of the element obtained for both samples was almost similar to the nominal stoichiometric of BCZY; Ba= 1.00, Ce= 0.54, Zr= 0.36, Y= 0.10 indicate that additional of Brij97 in the system does not alter the elemental composition of the final product.

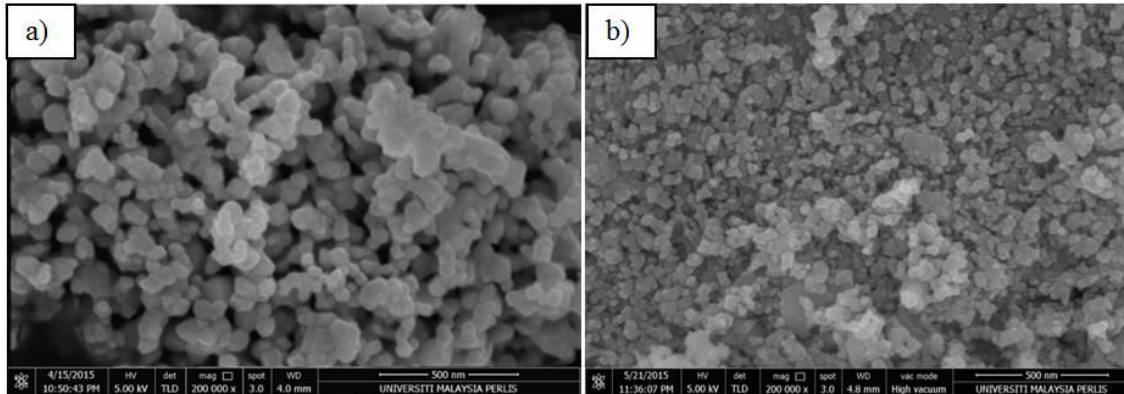


Figure3: SEM images of prepared powders calcined at 1100 °C. a) S1 and b) S2

Table 2: Elemental composition of prepared samples

Element	Sample/ Elemental atomic percentage (%)	
	S1	S2
O	21.02	20.70
Y	2.86	3.20
Zr	13.44	13.44
Ba	41.02	40.83
Ce	21.66	21.83

CONCLUSION

A low temperature method for the preparation of $\text{BaCe}_{0.54}\text{Zr}_{0.36}\text{Y}_{0.1}\text{O}_{2.95}$ is reported. It is shown that the thermal decomposition of the dried sample was completed at $T < 1000$ °C for both samples. Sample prepared with surfactant (S2) successfully formed a single perovskite phase of BCZY at calcination temperature of 1100 °C. However, S1 exhibit a mixture of secondary phase of BaCeO_3 and BaZrO_3 respectively. SEM analysis revealed that S2 consists of less aggregation with better dispersion between particles compared to S1. The addition of Brij97 did not give any significant effect on the elemental composition of the obtained powder as shown in EDX analysis. Further study on the electrical properties of BCZY powder will be reported elsewhere.

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