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ROLE OF DIMETHYLDIOCTADECYL AMMONIUM CHLORIDE (DiDAC) AS CATIONIC SURFACTANT ON THERMAL DECOMPOSITION AND PHASE FORMATION OF $Ba(Ce,Zr)O_3$ CERAMIC POWDERS

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ABSTRACT

Ceramic powder of $BaCe_{0.54}Zr_{0.36}Y_{0.1}O_{2.95}$ (BCZY) was synthesized via a modified sol-gel method using metal nitrate salts as precursors. Dimethyldioctadecylammonium chloride (DiDAC), citric acid (CA) and ethylene glycol (EG) was employed as a cationic surfactant, chelating agent and polymerization agent, respectively. The prepared samples were designated as S1 (without surfactant) and S2 (with surfactant) and characterized by the thermogravimetric analyzer (TGA), and X-ray diffractometer (XRD). S2 exhibited lower thermal decomposition temperature (T_{td}) compared to S1, since there was no significant weight loss after 740 ºC as proven by TGA result. The reduction in T_{td} of S2 might due to the presence of hydrocarbon chain in surfactant molecules that act as fuel and helps in the combustion process. XRD result showed the formation of single-perovskite phase of $Ba(Ce,Zr)O_3$ for both of the samples after they were calcined at T= 1000 ºC (S2) and at T= 1100 ºC (S1). However, the addition of DiDAC did not give any significant effect on the unit cell volume of BCZY.

Keywords: Cerate-zirconate ceramic powder; modified sol-gel; cationic surfactant; thermal decomposition; phase formation

INTRODUCTION

Recently, proton conducting electrolyte materials have attracted much attention due to their great advantages over oxide ion conducting ones, such as higher ionic conductivity, lower activation energy and higher energy efficiency [1]. Solid solution based on cerate-zirconate such as $Ba(Ce,Zr)O_3$ have been intensively investigated due to their adequate proton conductivity and acceptable chemical stability in hydrogen and water vapor containing atmosphere as well as in CO_2 environment [2]. Conventionally,

$Ba(Ce,Zr)O_3$ powder was synthesized using a solid-state reaction (SSR) method which employed ball-milled, repetitive grinding with multiple calcination steps followed by long firing time. As a consequence, micro-homogenous phase structures are difficult to obtain, due to large and strongly bonded powder agglomerates [3]. A promising approach to overcome the SSR shortcoming is by employing a soft, wet chemical technique, which has the advantage of producing high crystallinity and homogenous ultra-fine powders at relatively low temperature. Most of the researchers adopted hydrocarboxylic acid (usually citric acid) in their study as the synthesizing aid to promote the homogeneity of the precursor [4, 5]. In this work, cationic surfactant was employed as a catalyst for further modification in the preparation of the cerate-zirconate solid solution.

Applying surfactants which are composed of molecules contains the hydrophilic and hydrophobic tails, along with sol-gel method can improve the properties of the synthesized powder. The addition of cationic surfactant with amphiphilic molecules into precursor solution results in the formation of reverse micelles in the gel. Placing the aqueous ions inside these micelles can be effectively in controlling the nucleation and the growth of the particles [6]. Nevertheless, the use of cationic surfactant in synthesizing cerate-zirconate ceramic powder is rarely documented. Thus, the aim of this study is to investigate the influence of DiDAC as a cationic surfactant on the thermal decomposition and phase formation of $BaCe_{0.54}Zr_{0.36}Y_{0.1}O_{2.95}$ solid solution.

EXPERIMENTAL

Ceramic powder of $BaCe_{0.54}Zr_{0.36}Y_{0.1}O_{2.95}$ was synthesized by a modified sol-gel method using raw materials based on nitrate salts as received namely $Ba(NO_3)_2$ (99%, ACROS), cerium(III) nitrate hexahydrate, $Ce(NO_3)_3.6H_2O$ (99.5%, ACROS), zirconyl(IV) nitrate hydrate, $Zr(NO_3)_2O.4.8H_2O$ (99.5%, ACROS), yttrium(III) nitrate hexahydrate, $Y(NO_3)_3.6H_2O$ (99.9%, ACROS), citric acid monohydrate (99%, Merck), ethylene glycol (99.96%, ACROS) and dimethyl dioctadecyl ammonium chloride (DiDAC, Adrich). The prepared sample was labeled as shown in Table 1. A stoichiometric amount of metal nitrates salts was first dissolved in 100 ml of deionized water. The metal nitrate solution was stirred until a transparent solution was obtained. The calculated amount of citric acid (CA) was added in the solution followed by cationic surfactant (DiDAC) under continuous stirring. Next, ethylene glycol (EG) was added to aid the polymerization process. The pH of the solution was adjusted to a neutral pH value by adding an appropriate amount of ammonium hydroxide solution. Then, the stirring and heating processes were controlled accordingly. After the solution turn into a black sponge-like materials, the gel was further dried in a furnace at T= 325 ºC with a heating rate of 10 ºC min^{-1} for 2 hours. The as-synthesized powder was calcined at 950 ºC, 1000 ºC and 1100 ºC to obtain light-yellow BCZY powder with heating rate of 10 ºC min^{-1} for 10 hours.

Table 1: Nomenclature for the prepared BCZY sample

Sample	Surfactant
S1	None
S2	DiDAC

The as-synthesized powder (T= 325 ºC) was characterized by a PerkinElmer thermogravimetric analyzer (Pyris Diamond). The sample was heated from room temperature to 1100 ºC with a heating rate of °C min^{-1} under synthetic air (flow rate 100 ml min^{-1}). The phases of calcined powders were verified by a Shimadzu X-Ray diffractometer (XRD) using Cu-Kα radiation (λ = 1.5406 Å) at 2Θ from 20° to 80° in a step of 0.02° and scanning time at 2.5s each step. The operation voltage and current were maintained at 40kV and 35mA, respectively. The lattice parameter for the single-phase sample was calculated using MathCAD 14 software.

RESULTS AND DISCUSSIONS

TGA analysis.

The TG curves of as-synthesized powders (T=325 ºC) were shown in Figure 1. Both samples exhibited almost similar decomposition behavior with three stages of weight losses. Stage 1 takes place in the range of 27~270 ºC with the weight loss of about 2~7 % corresponds to the dehydration of the absorbed moisture, decomposition of nitrate species and remaining of low boiling point (B_p) of the organic species [7]. At stage 2, the weight loss observed between 270~710 ºC with weight loss about 19~93 % attributed to the decomposition of residual oxidizer (nitrates) and the organic compounds such as citric acid, ethylene glycol and DiDAC. The apperance of the steep curve in this stage was due to the oxidation and combustion of chelated complexes and the burn-out of the residual surfactant in the sample. Water (H_2O), carbon dioxide (CO_2) and nitrogen- based gas (NO_x) was released as the chelating agent and surfactant used are the sources of carbon, hydrogen, oxygen and nitrogen.

The weight loss observed in stage 3 at ≈1000 °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. The S2 sample showed the temperature for the beginning of crystallization process was at T = 500 °C which is lower than S1 (T= 710 °C). This observation might due to the presence of a large number of carbon chains in DiDAC structure which helps to accelerate the decomposition reaction of the intermediate compound to form BCZY oxide ceramic powder. There is no further change in the weight loss after stage 3 indicates a complete removal of organic species in the samples. The summary of weight loss of both samples was presented in Table 2.

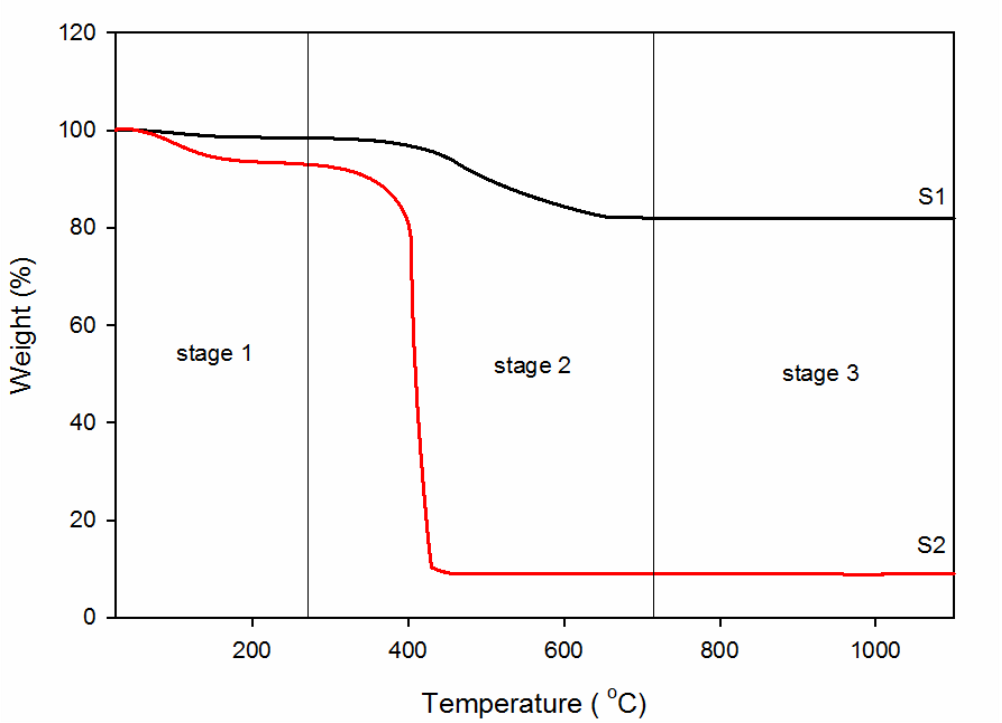


Figure 1: TG profile of the dried samples (T= 325 ºC) of S1 and S2

Table 2: Weight loss for dried powder (T =325 °C)

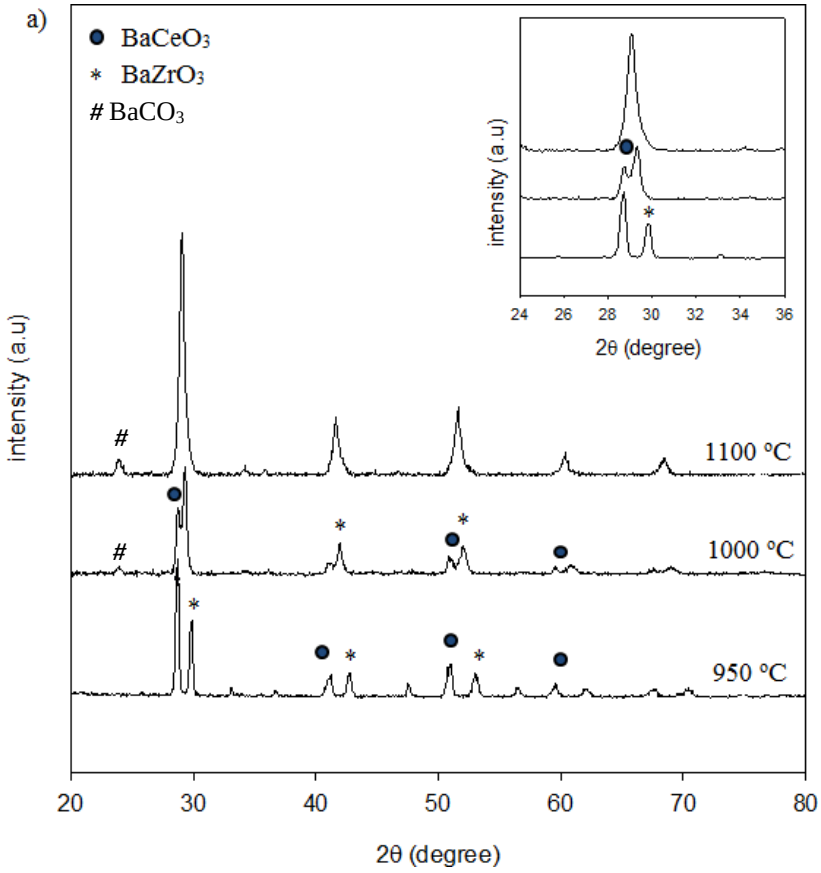
Sample	Stage	Temperature range [°C]	Weight loss [%]	Total weight loss [%]
S1	1	27-270	2	19
	2	270-710	16	
	3	710-920	1	
S2	1	29-260	7	93
	2	260-500	85	
	3	500-740	1	

XRD analysis.

The XRD patterns of the samples calcined at different temperatures was shown in Figure 2. At the calcination temperature of 950 ºC, S1 and S2 consist a mixture of $BaCO_3$, $BaCeO_3$ and $BaZrO_3$. It clearly shows that at T= 950 ºC, both samples exhibit incomplete reaction due to the insufficient energy to substitute Zr^{4+} ion into Ce^{3+} sites. As the calcination temperature increase to 1000 ºC, S2 sample (Figure 2(b)) successfully formed single perovskite phase of $Ba(Ce_{0.7}Zr_{0.3})O_3$ (JCPDS card no. 89-2485) with cubic structure. However, S1 sample only formed single perovskite phase of

BCZY after calcined at T= 1100 °C as illustrated in Figure 2(a) which is 100 ºC higher than S2.

This temperature reduction of S2 might due to the formation of reversed micelle in the solution during the addition of DiDAC in the synthesizing process. Due to the existence of surfactant, the surface tension of solution is also reduced, which reduces the energy of the formation of the new phase [6]. This result indicates that DiDAC could decrease the crystallization temperature of BCZY effectively which is align with TG data as shown in Figure 1. A work done by Wang et al., [8] also suggested that the formation of reverse micelle by the employment of cetrylammonium bromide (CTAB) in their study. The formation of micelle might induce a more stable metal complexes leading to the formation of BCZY at a lower temperature.



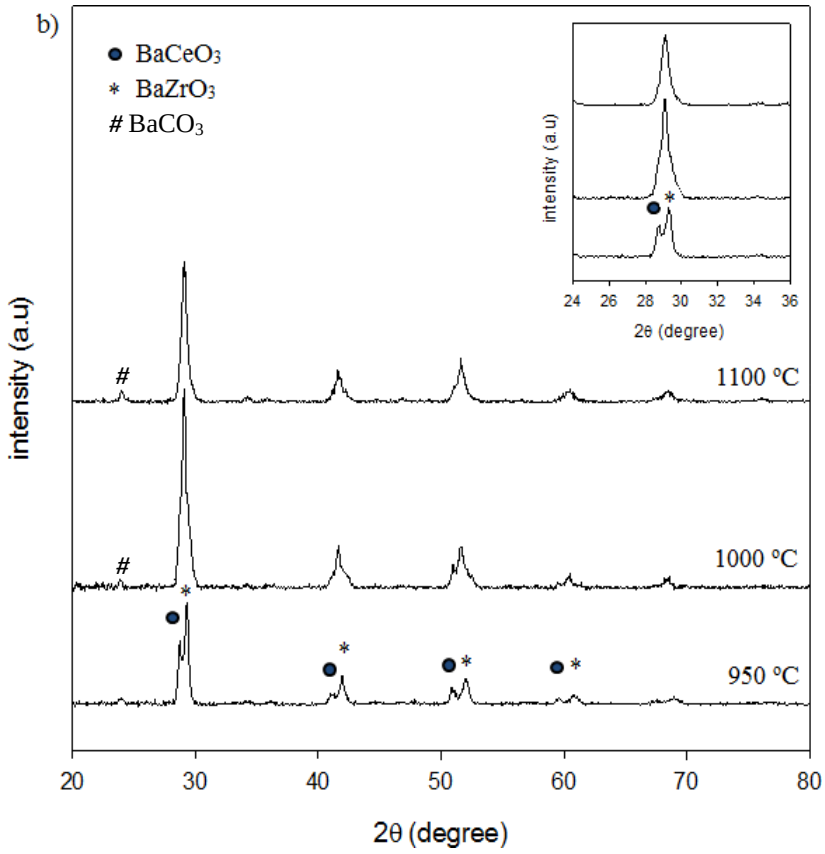


Figure 2: XRD spectra of calcined sample a) S1; b) S2. Inset: Enlarged peak of (110) indexed

Table 3: Reported values of the lattice parameter and unit cell volume of $Ba(Ce,Zr)O_3$

Compound	**Surfactant**	**Lattice parameter (Å)**	**Unit cell volume, V (Å)^3**	**Reference**
$BaCe_{0.8-x}Zr_xY_{0.2}O_{3-\delta}$	-	4.320	80.61	[9]
$BaCe_{0.8-x}Zr_xY_{0.2}O_{3-\delta}$	-	4.344	81.99	[10]
$BaCe_{0.54}Zr_{0.36}Y_{0.1}O_3$	-	4.338	81.55	[this work]
$BaCe_{0.54}Zr_{0.36}Y_{0.1}O_3$	DiDAC	4.332	81.35	[this work]

In addition, the lattice parameter and unit cell volume of BCZY phase are presented in Table 3. The lattice parameter calculated from XRD pattern of each sample showed almost similar value with the values reported in JCPDS database ($Ba(Ce_{0.7}Zr_{0.3})O_3$: JCPDS card 89-2485, a= 4.344Å). It shows that by the addition of DiDAC as a cationic surfactant during the synthesis process did not cause any surface reconstruction that may result in the deviation of lattice constants of BCZY from its mean theoretical value.

CONCLUSION

In this work, the preparation of $BaCe_{0.54}Zr_{0.36}Y_{0.1}O_{2.95}$ by a modified sol-gel method assisted with DiDAC as a cationic surfactant is reported. Thermal behavior of the dried samples (T= 325 ºC) exhibited the same decomposition behavior with three stages of weight loss. The S2 sample showed lower thermal decomposition temperature (T_{td}) compared to S1 due to the presence of hydrocarbon group in DiDAC which helps in the combustion process. XRD results confirm the formation of single perovskite phase of BCZY was obtained at T= 1000 ºC for S2 which is lower compared to S1 (T= 1100 ºC). The reduction of calcination temperature about 100 ºC with the presence of DiDAC showed that the employment of surfactant is very a promising approach in preparing this type of ceramic. Moreover, the results of lattice parameter obtained showed that DiDAC has no influence on the contraction or expansion of lattice unit cell volume. Further study on morphology and particle size will be reported elsewhere.

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