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Short Communication

Chelating Agents Role on Thermal Characteristics and Phase Formation of Modified Cerate-Zirconate via Sol-gel Synthesis Route

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Powder of $BaCe_{0.54}Zr_{0.36}Y_{0.1}O_{2.95}$ (BCZY) was synthesized by a modified sol-gel method. Glycolic acid, citric acid, triethylenetetramine (TETA), nitriloacetic acid (NTA) and ethylenediaminetetracetic acid (EDTA) were used as chelating agents. The role of chelating agents on the phase formation and thermal characteristics of ceramic powders has been investigated. The obtained powders were characterized by employing thermogravimetric analysis (TGA), Fourier transform Infrared (FTIR) spectroscopy and X-ray diffractometer (XRD). Thermal decomposition of the samples was about to complete at ≈ 950°C based on the TG-DTG profile. FTIR spectra detected the trace of carbonate residue in all samples and XRD pattern showed high intensity of perovskite phase formed for sample prepared with TETA. It was found that TETA is the best chelating agent with metal nitrate salts as precursors to produce a pure phase of BCZY powders at 1100 °C.

Keywords: perovskite-type oxide, sol-gel, chelating agents, thermal characteristics, TETA

1. INTRODUCTION

Perovskite-types oxides based of cerate-zirconate are well known as ions conductor at intermediate temperature in atmosphere containing hydrogen and/or water vapor. These materials have received much attention due to the low activation energy and high conductivity compared to other perovskite compounds [1-3]. The properties of cerate-zirconate are known to have strong depended on the sample preparation techniques and had conventionally been prepared by solid state-reaction (SSR) method. In this method, the starting materials were mixed stoichiometrically, ball milled, ground and fired at high temperature. Although the method employed is straight forward but it led to several disadvantages on the powder properties such as in-homogenous particle size and agglomeration [4-6].

High temperature sintering is a time and cost consuming. Thus, a promising approach to reduce high temperature sintering is the used of wet chemical methods (WCMs). This method is able to lower the calcination and sintering temperatures as well as synthesizing time. In addition, the homogeneity of the final product increases due to the mixing of the reagents occurs at the molecular level. WCMs consist of several routes such as co-precipitation, combustion, sol-gel, gel-casting, Pechini method, etc [7-9]. Among these techniques; a sol-gel method is one of the most attractive synthesis routes for preparing cerate-zirconate powder with homogeneous metal ions distribution at atomic level as well as lowering the synthesis temperature. In sol-gel processes, the hydrolysis and condensation reactions of molecular precursors are carried out in a controlled manner in order to obtain homogeneous gel.

Although this method lowered the processing temperature, additional phases of $BaCO_3$ still presence as impurities even after calcined at 1100 ^oC [10, 11]. The existence of $BaCO_3$ which is thermodynamically a very stable compound is the major factor that weaken the solid barium cerate mechanical integrity[12]. Thus, the formations of $BaCO_3$ need to be avoided in sustaining the properties of ceramics powder. On the other hand, this high temperature processing results in large particle aggregation and growth which is not suitable for the preparation of nanopowders.

Recently, many researchers work on the using of different chelating agents to avoid or hindered the formation of $BaCO_3$. The differences in chelating strength give different interaction during chelation process. Chelation is the formation of bonding between two or more separate binding sites within the same ligand and a single central atom. Usually this ligand is organic compounds and called chelants, chelators, chelating agent, or sequestering agents. The regularly used chelating agents are those that coordinating the metal ions through oxygen atom but recently, considerable attention has been devoted to study the chelating agent that can coordinate through nitrogen donor atoms or through both.

In this work, five different chelating agents consisting different donor atom used to synthesize cerate-zirconates powders; glycolic acid, citric acid, triethylenetetramine (TETA), nitriloacetic acid (NTA), and ethylenediaminetetracetic acid (EDTA). The aim of this work is to study the effects of different chelating agents on the thermal decomposition behavior and phase formation of synthesized powder. The chelation process between chelating agent and metal cation was investigated by thermal analysis (TG/DTG) and Fourier transform infrared (FTIR) spectroscopy and the phase formation of samples was confirmed by X-Ray diffraction (XRD).

2. EXPERIMENTAL

Cerate-zirconate compound with formulation of $BaCe_{0.54}Zr_{0.36}Y_{0.1}O_{2.95}$ was prepared with five different chelating agents (CA) via a modified sol-gel method using metal nitrate salts as starting materials. The CA used was glycolic acid (99%, ACROS), citric acid monohydrate (99%, Merck), Triethylenetetramine (60%, ACROS), nitriloacetic acid (99%, ACROS) and Ethylenediaminetetracetic acid (99%, ACROS). Ethylene glycol (99.96%, ACROS) was used as esterification agent. The molar ratio of CA to ethylene glycol and metal cation was fixed at 3:2:3.

A stoichiometric amount of $Ba(NO_3)_2$ (99%, ACROS), $Ce(NO_3)_3.6H_2O$ (99.5%, ACROS), $Zr(NO_3)_2O.xH_2O$ (99.5%, ACROS) and $Y(NO_3)_3.5H_2O$ (99.9%, Aldrich) was dissolved in deionized water and continuously stirred on a hot-plate to make a transparent nitrate solution. During stirring, the respective chelating agents were slowly added into metal nitrate salts solution. But for NTA and EDTA, the chelating agent has to be dissolved in ammonium hydroxide in order to promote the dissolution of the chelating agent in deionised water, then the solution was gradually added into metal nitrate salts solution [13, 14]. The mixture produce from glycolic acid denoted as A1, for citric acid as A2, TETA as A3, NTA as A4 and EDTA as A5. Ethylene glycol then added into the complex solution to adjust the viscosity of the solution and control the moving velocity of the metal ions, resulting in the gelation of reaction mixture [15]. A concentrated ammonia solution was used to neutralize the complex solution. The resulting solution was slowly evaporated on a hot plate at 120 ^oC. The heating and stirring process was control accordingly. During the process, the browning gas (known as NO_x) was released and a dark brown gel obtained. The gel was dried at 325 ^oC in a furnace to yield yellow fine flakes. Then the sample was calcined at 1100 ^oC with heating rate of 10 ^oC min^{-1} for 10 h to produce light-yellow powder.

Thermogravimetric analysis (TGA) was carried out to the dried powder (T= 325 ^oC) by a TA instrument model SDT Q 600. Fifteen milligrams of dried powder was placed in an alumina pan and heated from 25 to 1000 ^oC with a heating rate of 10 ^oC min^{-1} under synthetic air (flow rate 100 ml min^{-1}), and the sample weight change was recorded as a function of temperature. IR spectra were recorded with a FTIR spectrometer (Nicolet 380) in the range 400 – 4000 cm^{-1} to investigate the complex, carbonates and oxides formation. The phase of calcined powders was verified by a Shimadzu X-Ray diffractometer (XRD) using Cu-K_α radiation (λ= 1.5406 Å) from 20^o to 80^o in step of 0.02^o at 2θ.

3. RESULTS AND DISCUSSIONS

3.1. Thermal analysis

Figure 1 shows the thermal decomposition characteristics of the dried powder (T=325 ^oC) prepared using five different chelating agents. All the TG curves exhibit three stages of weight loss but only two stages for A4. The first stage of weight loss, ≈8% appears between 27 – 240 ^oC, is attributed to the drying process; evaporation of coordinated and solvent water. This is also related to the complete chelation process with the loss of NO_x gaseous.

The second stage of weight loss occurs in range 240 – 600 ^oC which the TG profile is practically similar for all samples. The major weight loss resulting from the decomposition of residual oxidizer (nitrates) and the organics (i.e. glycolic acid, citric acid, TETA, NTA, EDTA) in the precursors resulting in the sharp exothermic peak in DTG curve. Such behavior may be due to the oxidation and combustion process of the carboxyl metal group and nitrate group result in the liberation of gases such as CO_2, H_2O and NO_2. Upon treatment, free water escaped from the surface of the powders and then the organic residues oxidized to CO_2 and H_2O. The detailed molecular interaction and their mechanism are still under investigation and will be reported elsewhere.

The last stage of thermal decomposition arises from the decomposition of the trapped carbonates residues, which are formed as intermediate products. This is also referred to the beginning of the crystallization as well as the structural transformation to form metal oxides.

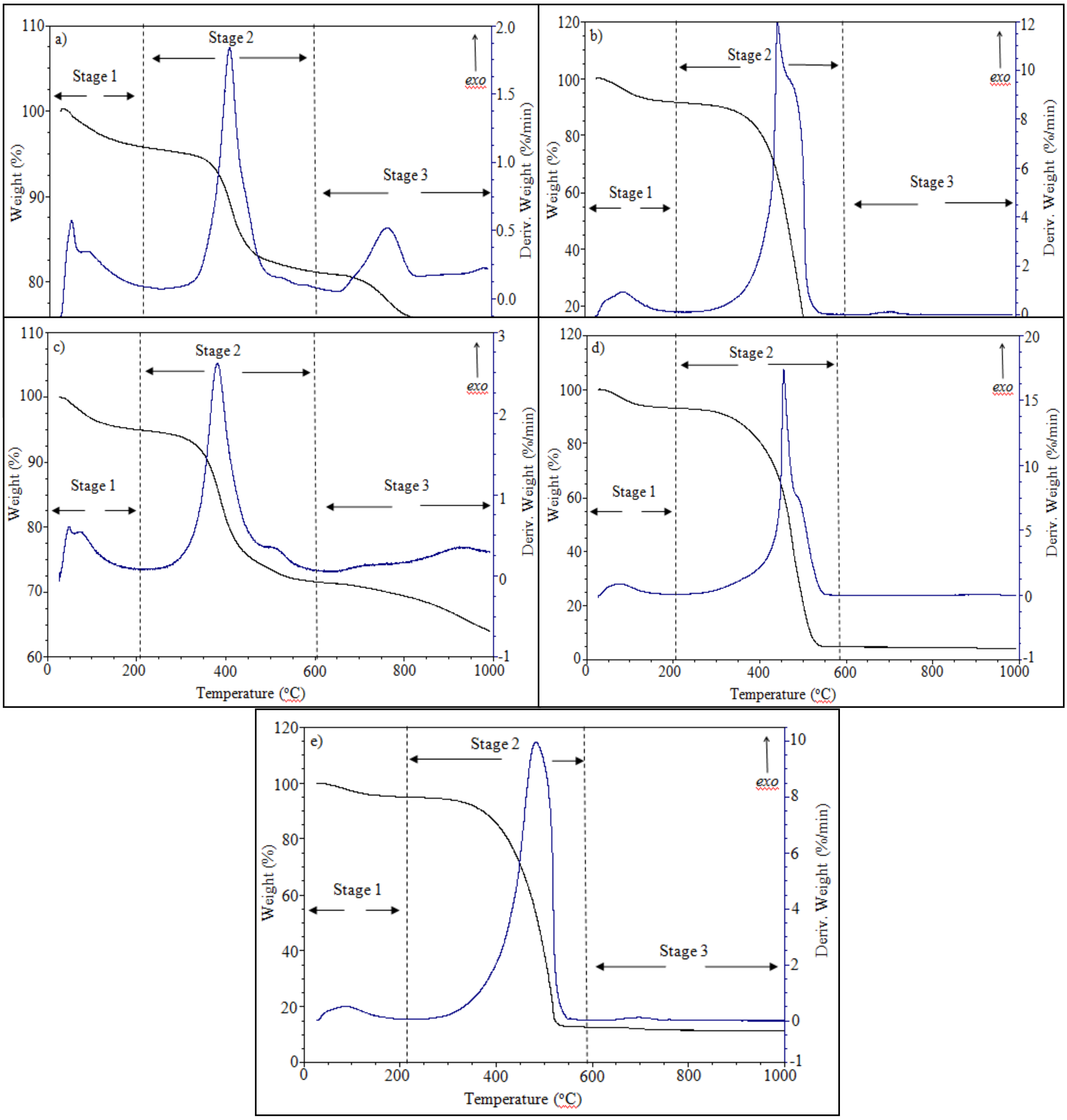

Figure 1. TG thermograms of dried powder (T=325 °C) for a) A1, b) A2, c) A3, d) A4 and e) A5.

Table 1 showed the summarization of the thermal characteristics of dried powder (T=325 ^{o}C) for A1, A2, A3, A4 and A5. The total weight loss when the precursors converse to oxide is different for each sample. This is due to the molecular weight of the chelating agents used to prepare the powder. High molecular weight of the chelating agents used results in the great amount of organics to be removed [16, 17]. The amount of the excess organic decreases in the order: EDTA>citric acid>NTA>TETA>glycolic acid and this is in line with their molecular weight 292 g/mol>210 g/mol> 191 g/mol> 146 g/mol> 76 g/mol. Hence, the temperature profile for heat treatment should be carefully design to allow a uniform removal of excess organics and it is found that the thermal behaviors of BCZY are influenced by the different types of chelating agents used.

Table 1. The summarization of thermal characteristics for dried powders (T= 325 ^{o}C)

Sample	Stage	Temperature range (^{o}C)	Mass loss (%)	Total mass loss (%)
A1	1	27 – 240	4	
	2	240 – 590	15	28
	3	590 – 980	9	
A2	1	27 – 240	8	
	2	240 – 540	85	94
	3	540 – 780	1	
A3	1	27 – 220	5	
	2	210 – 570	23	35
	3	570 – 950	7	
A4	1	27 – 230	7	
	2	180 – 570	85	92
	3	-	-	
A5	1	27 – 240	4	
	2	240 – 610	85	96
	3	610 - 750	1	

3.2. FTIR Analysis

FTIR spectra for all samples after treated at 325 ^{o}C, and 1100 ^{o}C, respectively is shown in Figure 2. For dried powder, there are several regions of spectroscopic interest involving the C=O (in COOH), C-OH (carbon bonding to alcoholic OH) and metal-oxygen bonding. The peaks localized at ~ 1699 – 1623, ~1400, ~1586, ~1322 cm^{-1} are related to the symmetric and asymmetric of carboxylate stretching mode for a complex formed from a chelation process of chelating agents and metal ions. The bands at ~1114, ~ 857 and 692 cm^{-1} are assigned to the carbonate ions (CO_3^{2-}). The absorption bands appear in the spectra because some of the CO_2 molecules are adsorbed on the powders. The vibration of metal-oxygen in intermediate resin as represented by small peaks at ~ 500 cm^{-1} indicates the chelation process has occurred.

As the calcination temperature increased to 1100 ^{o}C, the bands associated to the –OH vibration and other organic compounds become weaker and the vibration bands of metal-oxygen at ~ 488 cm^{-1}

become stronger. The possibility of metal oxide formation may predict at this calcination temperature. However, it was found that a low transmittance intensity of carbonates peaks is present in the spectra. There were two possible approaches the carbonate contamination can be formed. First, the carbonate ions were influenced by the incomplete combustion of the chelating agents that contains carboxylic group. The carboxylic group burnt out and form carbonates ions. The possible reaction equation of the combustion process between the chelating agents that consists of carboxylic group can be written as the Reaction 1. During the heat treatment, the byproducts formed which is carbonate will possibly reacts with Ba^{2+} to become $BaCO_3$.

$$Ba(NO_3)_2 + 0.1Y(NO_3)_3{\cdot}6H_2O + 0.54Ce(NO_3)_3{\cdot}6H2O + 0.36Zr(NO_3)_2O{\cdot}5H_2O + C_6H_8O_7{\cdot}H_2O + C_2H_6O_2 + 2NH_4OH + 8.5O_2 \rightarrow BaCe_{0.54}Zr_{0.36}Y_{0.1}O_{2.95} + 8CO_2 + 13H_2O + N_2 \quad \ldots\ldots\ldots\ldots\ldots\ldots(1)$$

High temperature is needed to break the $BaCO_3$ bond because it is thermodynamically most stable compounds. Charroborty et al.[18] reported that the temperature as high as 1300 °C was needed to eliminate the small traces of $BaCO_3$ for the $BaCe_{0.8}Sm_{0.2}O_3$ sample.

For A3, the chelating agents used does not contain any –COOH groups, however a small intensity for unrequired peak at 1439 cm^{-1} is still presence in the spectra suggests that the carbonates were presumably formed due to the reaction with CO_2 in the atmosphere during calcination process.

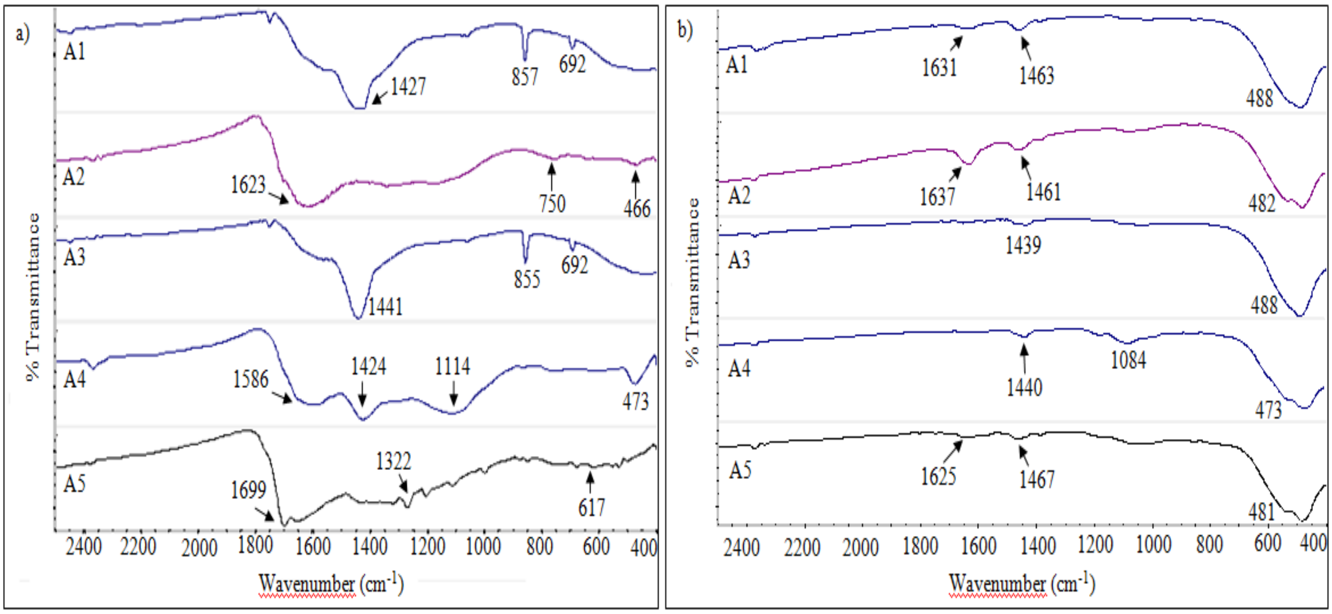

Figure 2. FTIR spectra for a) dried powder (T=325 °C) and b) calcined powder (T=1100 °C)

3.3. XRD Analysis

The formation of cerate-zirconate phase was confirmed by XRD measurement as shown in

Figure 3. For A1, A2, A4 and A5, the XRD diffraction pattern showed a mixture of respective $BaCeO_3$ and $BaZrO_3$ phases. The present of the phases are due to the chelating agents used where NTA is one of the least stable amino polycarboxylics acid towards the chelation process. Therefore, high temperature was needed to enhance the substitution of Zr^{4+} into Ce^{3+} site and eliminate the $BaCO_3$ phase to produce pure phase of BCZY powders.

A3 showed high intensity and narrow peak perovskite phase of BCZY powders. At calcination temperature of T= 1100 ^{o}C, A3 formed the cubic barium cerate-zirconate of $BaCe_{0.54}Zr_{0.36}Y_{0.1}O_{2.95}$ formulation. The pronounce peaks can be indexed to (110), (111), (200), (210), (211), (220) and (310), respectively however the appearance of the small remnant of carbonates was still detected at $2\theta \approx 26°$. This result is in agreement with the FTIR spectra that showed the carbonates traces at ~ 1439 cm $^{-1}$. The high intensity of the perovskite phase formed might be due to the role of TETA as chelating agent since its structure does not contain –COOH group.

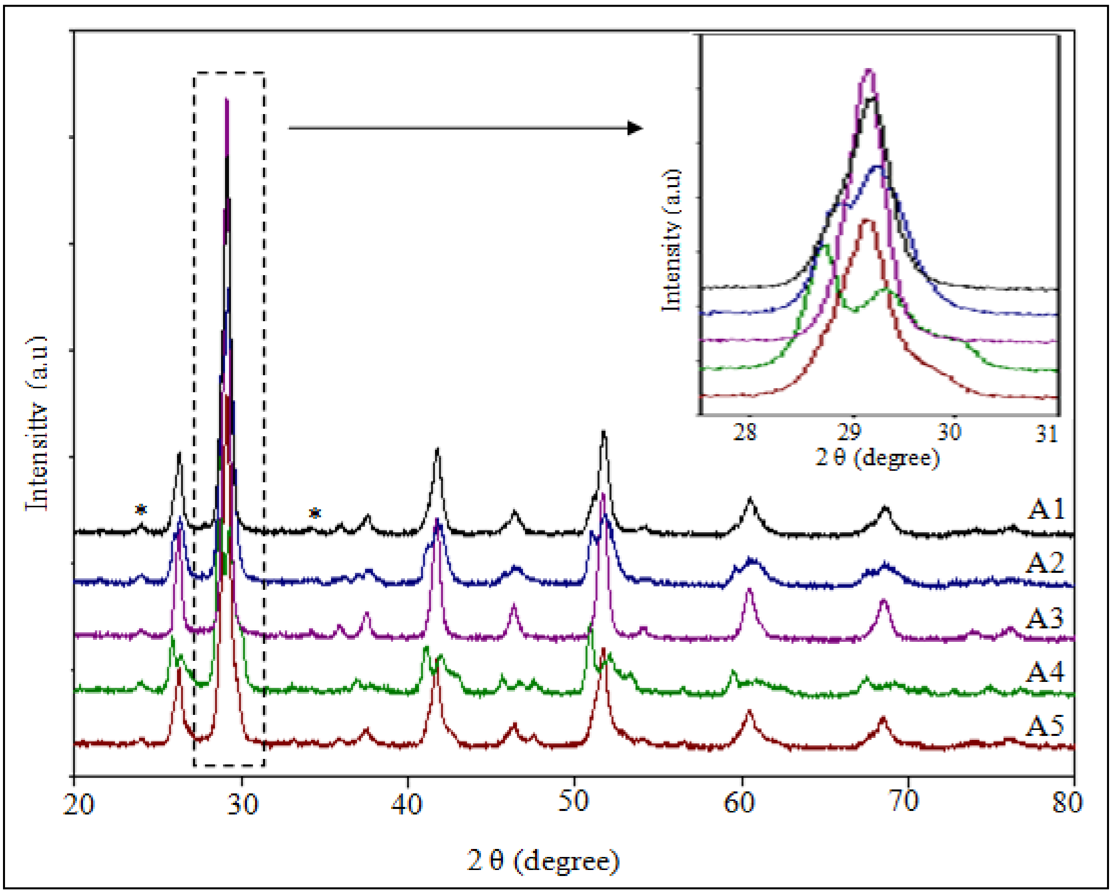

Figure 3. XRD spectra for BCZY powders after calcined at T=1100 ^{o}C.

TETA possesses four functional amine groups; two of them locate at each head position and the others insert in the chain structure. TETA exhibits strong coordinating ability towards metal ions due to the electron-donating activity of amine groups with a lone pair of electrons in nitrogen [19]. In a mild solution-based surrounding, TETA primarily coordinates with the metal ions and lead to the homogeneous distribution of the constituent ions in the gel and enhance the crystallization process during heat treatment. High intensity of perovskite phase using TETA as chelating agents suggest the complete substitution of Zr at Ce sites via N-coordination of TETA to the cationic species at T=1100 °C. This results is also in-line with the work by Prostomo et al [20]. They found that the single phase of $BaZrO_3$ perovskite structure was enhanced when calcined from 1000 °C to 1100 °C using TETA as a chelating agent.

Table 2 shows a comparison of the method, chelating agents and calcination temperature used in obtaining pure phase of cerate-zirconate powder reported by the other researchers.

Table 2. Comparison of calcinations temperature used in obtaining pure-phase of cerate zirconate

Compound	Method	Chelating agents	Calcinations temperature (°C)	Ref
$BaCe_{0.76}Zr_{0.19}Yb_{0.05}O_{2.975}$	Pechini	Citric acid	1400	[21]
$BaCe_{0.65}Zr_{0.20}Y_{0.15}O_{3-\alpha}$	Microwave-assisted-sol-gel Pechini	EDTA	1400	[22]
$Ba(Zr_{0.89-x}Ce_xY_{0.2})O_{2.9}$	Glycine-nitrate combustion	Glycine	1400	[23]
$BaCe_{0.54}Zr_{0.36}Y_{0.1}O_{2.95}$	Sol-gel	TETA	1100	[This work]

4. CONCLUSION

A high purity of $BaCe_{0.76}Zr_{0.19}Yb_{0.05}O_{2.975}$ was successfully prepared via modified sol-gel method using TETA as chelating agents. The usage of TETA as chelating agents effectively reduces the formation of $BaCO_3$ in the final powders. As a result the single perovskite phase of BCZY powders was obtained at calcination temperature T= 1100 °C as confirmed by XRD results. TGA and FTIR results showed the used of TETA as chelating agents does not lead to the excessive amounts of carbonaceous contents. The role of TETA as chelating agents sheds a new light for the development of synthesizing $Ba(Ce,Zr)O_3$ at relatively low temperature. Further study on the morphologies and properties of the BCZY powders prepared with TETA is still in progress and will be reported elsewhere.

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