

THE DECOMPOSITION OF $\text{BaCe}_{0.95}\text{Yb}_{0.05}\text{O}_{2.975}$ PREPARED BY DIFFERENT PREPARATION ROUTES

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ABSTRACT

The oxidation behaviour from different metal salts influenced the formation of oxide ceramics. Three different preparation routes namely, solid state reaction (SSR), sol-gel (SG) and modified Pechini (PM) were used to synthesize a compound of $\text{BaCe}_{0.95}\text{Yb}_{0.05}\text{O}_{2.975}$. The thermal decomposition behaviour of this compound was carried out using thermogravimetric analysis (TGA). The thermal decomposition for SG and PM occurred in three stages but only two stages for SSR as shown in thermogravimetric (TG) signal. The exothermic reaction process to form oxide compound was shown by the derivative thermogravimetric (DTG) signal. The calcined powders at $T=1000^{\circ}\text{C}$, 1100°C and 1300°C by different routes were also analyzed by Fourier transform infrared spectrometry (FTIR) to identify the traces of carbonate species.

INTRODUCTION

Technique of sample preparation plays an important roles in preparing protonic conductor ceramic materials. The simple method to synthesize these ceramic compounds is by using SSR [1-5,9] technique. Wet chemical methods (WCMs) such as sol-gel (SG) [6-9] and modified Pechini methods (PM) [8,9] have proven better than SSR in producing powders with highly crystallinity and homogeneous fine at low temperature. Thermogravimetric analysis/differential scanning calorimetry (TGA/DSC) analysis is widely employed technique for measuring the change in weight of a sample as a function of temperature or time in controlled atmosphere. Fourier transforms infrared spectrometry (FT-IR) is powerful technique to identify the types of organic compound.

In this work, we have prepared $\text{BaCe}_{0.95}\text{Yb}_{0.05}\text{O}_{2.975}$ sample by using SSR method and two typical wet-chemistry synthesis methods namely SG and PM method. TGA/DTG and FT-IR analysis were used to investigate the thermal behaviour of sample that was prepared by different routes.

METHODOLOGY

Preparation Sample

SSR

High purity of BaCO₃, CeO₂, Yb₂O₃ were used as starting materials. All the materials were mixed and manually ground in an agate mortar with pestle and then calcined at 1300°C for 12 h.

SG

High purity of Ba(CH₃COO)₂, Ce(CH₃COO)₃.xH₂O and Yb(CH₃COO)₃.xH₂O were used as starting materials.

Each powder was dissolved in three different containers with certain solvent solution. The solutions were mixed together in a three necks round bottom flask until homogenous and then refluxed at 60°C for 2 hours under a continuous stirring. Then, a sufficient amount of citric acid was added into the resulting solution as chelating agent. The pH of the resulting mixture was changed from ≈3 pH to 6.5 by adding a concentrated ammonia (NH₄OH) solution. The solution was heated at 120°C for 5 hours to produce a dark brown gel. A sponge was formed after the gel was heated at 300°C for 5 h. Then, the sponge was ground in an agate mortar with pestle and the resulting powder was calcined at 1100°C for 12 hours. A detail preparation procedure of the sample using this method was reported by Osman et al. [6].

PM

High purity of Ce(NO₃)₃, BaN₂O₆ and Yb(NO₃)₃.5H₂O were used as starting materials. Citric acid monohydrate in 3:1, and ethylene glycol in a 3:2 molar ratio with respect to the total amount of cations were prepared. Citric acid acted as a complexing agent and ethylene glycol aided the polymerization process.

Stoichiometric amounts of metal nitrate salts were dissolved in deionized water under continuously mild stirred to make a transparent nitrate solution. Citric acid monohydrate was first added into the nitrate solution under continuous stirring. Then ethylene glycol was gradually dropped into the quartz beaker. The resulting solution was stirred over night. Then, the solution was heated at 120°C and stirred continuously for 2 hours using hot plate and a magnetic stirrer. During the process, most of the water evaporated yielding a viscous clear solution of metal-citrate complexes. By further heating, the clear solution became cloudy and then changed to yellow colored. After a while, browning gases were released and the solutions become a dark brown gel. The gel was heated at 300°C on a hot-plate overnight and transformed to a dark grey sponge-like.

A detail information of sample preparation was reported elsewhere by Osman et al. [8]. The compound was ground in an agate mortar then was pre-calcined at 550°C for 5 h. The compound was calcined at 1000°C for 12 h to ensure the entire organic compounds were burn out.

Sample characterizations

The thermal decomposition of dried powders (300°C) were analyzed using TGA/DSC model SDT-Q600. The powder was placed in an alumina cup and heated from room temperature to 1,400°C in air with heating rate of 10°C min⁻¹. Then the selected calcination temperature for sample powder was chosen based on TGA/DSC results. FT-IR was carried out to the calcine powder in order to identify that the existence of organic compounds in the sample. Amount of KBr and sample powder was mixed by ratio 1:100. The resulting compound was pelletized by using a manual hydraulic hand press.

RESULTS AND DISCUSSION

TGA/DSC analysis

Figure 1 shows the thermal decomposition of the dried powder prepared by SSR (pretreated at T=300°C). Two exothermic peaks at 800≤T°C≤1100 that were associated referred to the liberation of CO followed by CO₂ to yield oxide compound. The total weight loss of sample was about 13% and occurs in 2 stages. TG signal becomes flat at 1250°C indicating that the minimum calcination temperature was about 1300°C.

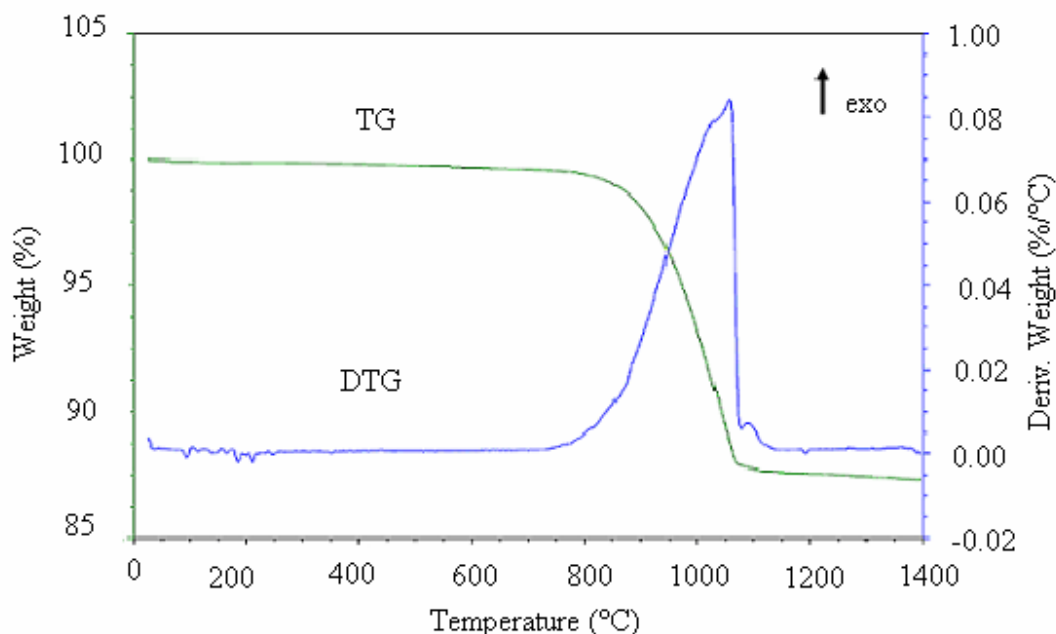


Figure 1: TG-DTG curves of the dried powder prepared by SSR.

Figure 2 shows the DTG and TG signals for the dried powder that prepared by SG method (pretreated at T=300°C). There are three significant stages of weight loss of the powder. Each stage was parallel by one or two exothermic peaks in DTG signal. All the stages resulted to the total weight loss of 17%. The first step, at T<200°C, is mainly due

to the lost of absorbed moisture and low boiling organic species that clearly shows by single pronounced exothermic peak at 82°C. Small weight loss from 400°C to 700°C in step two as shown by a small exothermic peak (or hump) was attributed to the liberation of high boiling organic residues. The third stage at $750 \leq T^{\circ}\text{C} \leq 1100$ mainly due to the liberation of CO followed by CO₂ to yield oxide compound. The thermal decomposition completed at temperature above 1000°C as also proved by the DTG signal. The used calcination temperature was about 1100°C for this sample.

Figure 3 shows the stages of thermal decomposition of the dried powder prepared by PM method (pretreated at T=300°C). About 70% of total weight loss occurs between the temperatures of 200°C to 450°C. Three main exothermic peaks were observed indicating that there are three significant weight loss in the sample. Su et al. [10] also reported that there were three stage of weight loss for BaCe_{0.8}Y_{0.2-x}O_{3-δ} prepared by Pechini method based on nitrate and oxides metal. The first peak at T<200°C, is mainly due to the loss of absorbed moisture and low boiling organic species. Vaporization of high boiling organic residues to form carbonate compounds was shown by a broad exothermic peak (or hump) at T=300°C. A peak between 350°C to 400°C is attributed to the liberation of CO from a carbonate compound. A pronounced peak at 430°C corresponds to the further decomposition of the compound, by releasing CO₂, to yield oxide compound. At temperature 1000°C, the TG and DTG signals become flat indicating that the decomposition is completed. The used calcination temperature for this sample was at 1000°C.

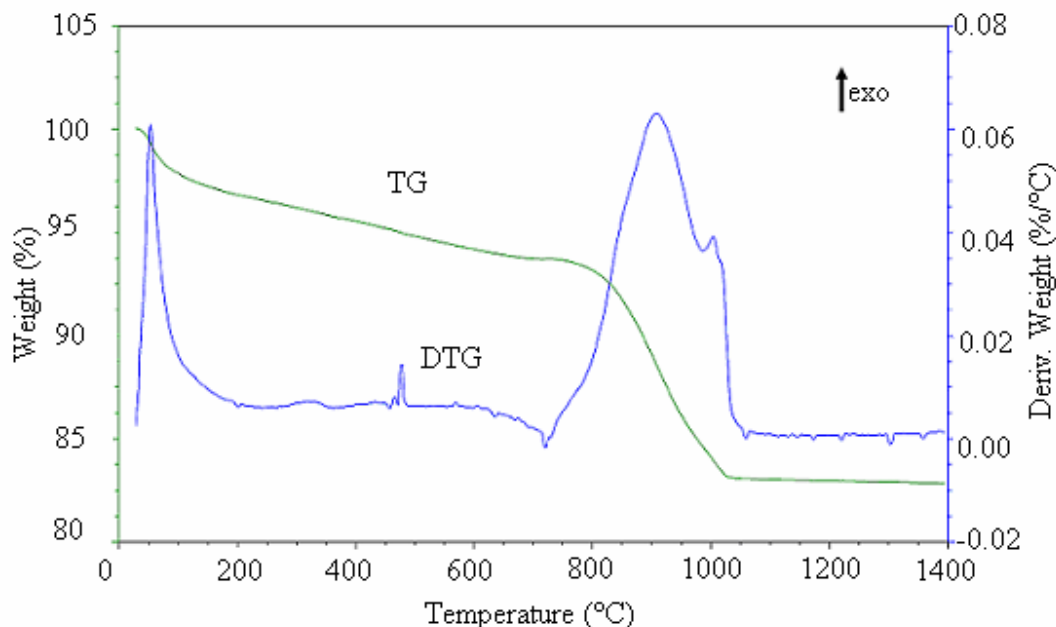


Figure 2: TG-DTG curves of the dried powder prepared by acetate route.

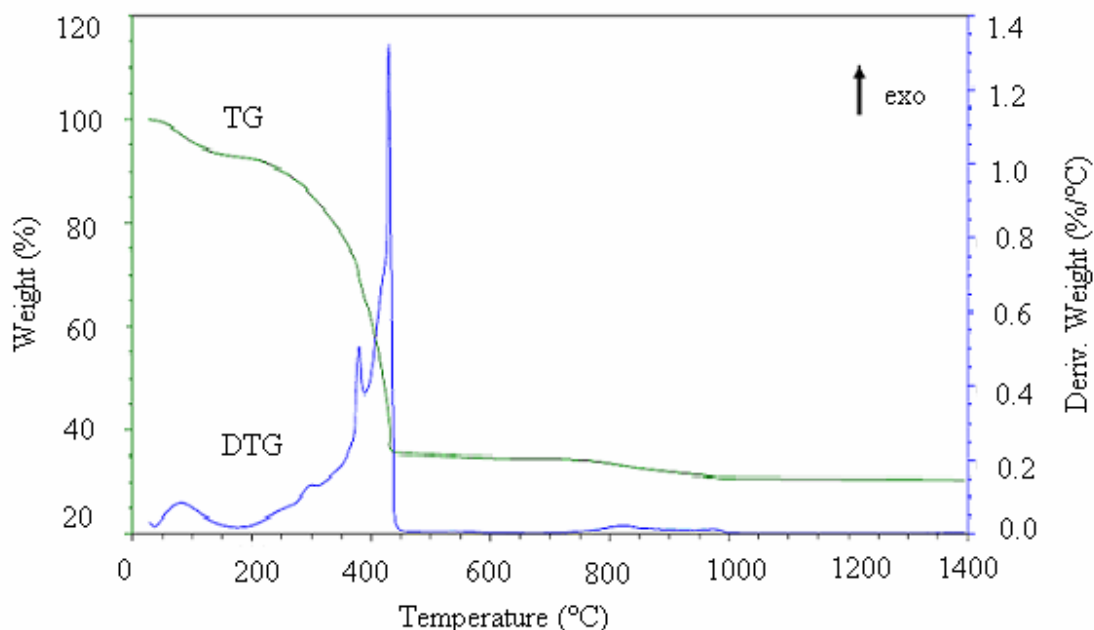


Figure 3: TG-DTG curves of the dried powder prepared by nitrate route.

Table 1: Summary of the decomposition process

Method	Total weight loss (%)	Absorbed moisture and low boiling organic species (°C)	High boiling organic residues (°C)	Liberation of CO (°C)	Liberation of CO ₂ (°C)
SSR	13	<300	-	1060	1150
SG	17	<200	300 ≤ T ≤ 650	910	1050
PM	70	<200	200 ≤ T ≤ 350	390	430

The decomposition temperatures of moisture, organic species, CO and CO₂ are shown in Table 1. It is found that the PM needs a lower temperature and the SSR method needs the highest temperature to formed oxide compound.

Generally all the carbonates base required higher decomposition temperature than the nitrates to oxide compound. For example, MgCO₃ decomposed to oxide compound at 540°C and MgNO₃ form decomposed at 400°C to be MgO. Moreover, in term of thermal stability, nitrate is unstable than carbonate. It means that nitrates are easier to decompose to be oxide material compared than carbonates.

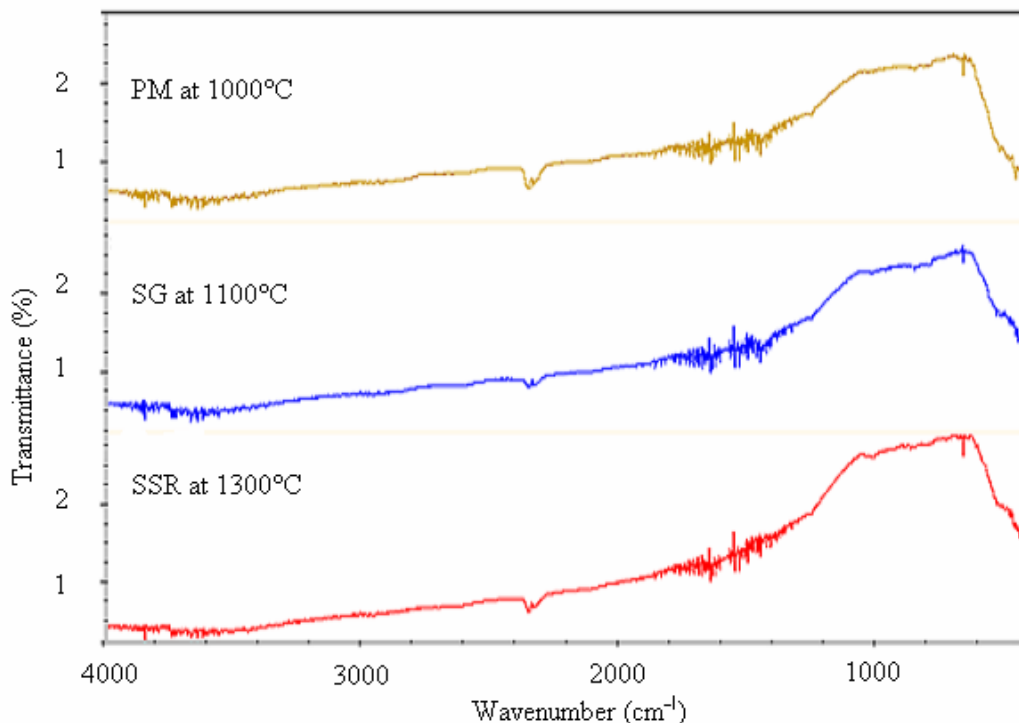


Figure 4: FTIR spectra of $\text{BaCe}_{0.95}\text{Yb}_{0.05}\text{O}_{2.975}$ that was prepared by different routes.

FT-IR

The FT-IR analysis was carried out after the powder was calcined at chosen temperatures depending on the results of TGA/DSC. Figure 4 shows the infrared spectrum of samples with different preparation methods. There were no absorption bands except a twin broadband at $\approx 2300\text{cm}^{-1}$ appeared in range $4000\text{-}400\text{cm}^{-1}$ for SSR, SG and PM methods after calcined at 1300°C , 1100°C and 1000°C , respectively. This broadband is associated to the artifact of the used instrument. Thus, we concluded that there were no traces of carbonate species residue such as BaCO_3 present in the sample. This observation is in agreement to the result of TG and DTG as shown in Figure 1-3.

CONCLUSION

A $\text{BaCe}_{0.95}\text{Yb}_{0.05}\text{O}_{2.975}$ compound was successfully prepared by three different routes that using different metal salts as precursor materials. Among the routes, PM method showed the highest percentage of total weight loss due to the decomposition, but needed a lower temperature to yield the oxide compound compared to SG and SSR method. It proved that metal nitrate salts showed better decomposition character than acetate and carbonate metal salts. FT-IR result confirmed that there were no traces or carbonate species in the final sample after they were calcined at 1300° , 1100°C and 1000°C for SSR, SG and PM methods, respectively. Further study will be reported elsewhere.

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