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SYNTHESIS OF Y^{3+}-DOPED $BaCeO_3$ BY SUPERCRITICAL ETHANOL USING HIGH-PRESSURE–HIGH-TEMPERATURE (HP-HT) BATCH WISE REACTOR SYSTEM

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ABSTRACT

A supercritical fluid technique was used to synthesize Y^{3+}-doped $BaCeO_3$ (BCY) ceramic compound by a High-Pressure–High-Temperature (HP-HT) Batch-Wise Reactor System. The samples were synthesized using ethanol as reaction medium at four different reaction temperatures with constant pressure. The respective prepared samples were denoted as C0, C1, C2 and C3. Chemical bonding of the reaction product was determined by a Fourier transform infrared (FT-IR) spectroscopy. All the calcined powder formed single perovskite phase of $BaCeO_3$ (JCPDS card 822425) as proven by X-ray Diffractometer (XRD). C0 and C1 were free from impurity as transmittance peak associated to the carbonate phase was not detected in the FTIR spectrum. However, traces of carbonate residue were detected for C2 and C3 samples which indicate the incomplete reaction of the intermediate compounds. Therefore, it is found that the low reaction temperature during the synthesizing process gives better characteristics of BCY ceramic powder compared to high reaction temperature of ethanol.

Keywords : Supercritical fluids; ceramic perovskite-type oxides;

INTRODUCTION

Solid oxide fuel cell (SOFC) is an energy-converter device of great industrial interest due to its high efficiency, low pollution and fuel flexibility [1]. The $BaCeO_3$ based material is one of the most promising electrolytes for intermediate temperature SOFC because of its outstanding proton conductivity [2,3]. The commonly used method to prepare the samples is via solid-state reaction (SSR). In this method, the starting materials are mixed in a stoichiometric ratio and directly ball-milled, ground and fired at high temperatures (T > 1400 ˚C). However, the milling and grinding processes introduced contaminates from abrasive materials. A promising approach to reduce high temperature processing is the use of wet chemical methods (WCMs). WCMs consist of several routes such as co-precipitation, combustion, sol-gel, gel-casting, Pechini method, etc [4-8]. It has been proven that WCMs can produce powders with high degree

of crystallinity and homogeneous nanopowder. On the other hand, they still possesses several limitations such as long reaction time and contamination with carbonate impurities.

Therefore, in order to overcome these problems, another method in synthesizing perovskite-type oxide materials is by using high pressure high temperature batch-wise reactor system at supercritical fluid state. Supercritical fluid technology has become an important tool of materials processing in the last two decades and being used extensively in preparing a great variety of nanomaterials. The selection of parameters particularly temperature and pressure in supercritical fluids has a great influence on the chemical nature of materials. The advantages of using supercritical fluids are short reaction time, minimize release CO_2 and avoid waste of solvent. In this present work, a high-pressure–high-temperature (HP-HT) batch-wise reactor system was used to synthesize Y^{3+}-doped $BaCeO_3$ (BCY) perovskite powder using ethanol as SCF media.

EXPERIMENTAL

Sample preparation

$Ba(NO_3)_2$(99 %, ACROS), $Ce(NO_3)_3.6H_2O$ (99.5 %,ACROS), and $Y(NO_3)_3.5H_2O$ (99.9 %, Aldrich) were used as starting materials for Y^{3+} doped $BaCeO_3$ without any further modification. Ethanol (95 %, HmbG) was used as solvent and reaction media. Each metal nitrate salt in stoichiometric amount was dissolved in ethanol. A mixture of the precursor materials was loaded inside a 350mL vessel and synthesised by a HP-HT batch-wise reactor system. The temperature and pressure of the solvent were controlled at various conditions using a controller as shown in Table 1. The amount of solvent depends on the percentage of liquid level filling or percent of reactor-free volume as reported by Ishak [9]. The facilities involved in monitoring the parameters are flow meters, temperature controller (thermocouple type-K located inside the vessel) and a back-pressure regulator (Unijin). After a fixed period of time, the vessel was transferred into a water bath to quench the reaction immediately. The obtained slurry was subjected to a vacuum suction to separate solid from the slurry. Rotary evaporator was used to evaporate the remaining solvent and the solid product was further calcined at 1100 °C at a heating rate of 10 °C/min.

Table 1: Denomination of BCY sample at different reaction temperatures with constant pressure (4 MPa)

Denomination of BCY Sample	Temperature (°C)
C0	150
C1	200
C2	250
C3	300

Sample characterization

The as-synthesized and calcined powders were subjected to the infrared spectroscopy analysis at room temperature using FT-IR Nicolet 380 spectrophotometer. The IR spectrum was used to observe the formation of metal oxide and the remaining carbonate ions as well as the intermediate compounds from 400 to 3,000 cm^{-1}. The phase identification of the samples was carried out by X-ray diffractometer (Shimadzu XRD-6000) equipped with Ni-filtered and graphite monochromatized Cu-K_α radiation (λ = 1.5406 Å) over a 2h range of 10˚ to 80˚ with step size at 0.02˚/s.

RESULTS AND DISCUSSION

Fourier transforms infrared spectroscopy (FT-IR)

The bonding characteristics of functional groups for the as-synthesised and calcined powders were identified by a FT-IR spectroscopy as shown in Figure 1. For the as-synthesised powders (Figure 1a), a small absorption band around 1776-1774 cm^{-1} for all samples are characteristic of absorbed water or hydroxyl group (O–H stretching) in ethanol. The characteristics of metal precursors bound to nitrate group (M-NO_3) for all samples are shown by two absorption peaks that appeared at 1418–1414 cm^{-1} and 1363–1386 cm^{-1} respectively [10]. The presence of a small sharp peak at 818–813 cm^{-1} indicates that the samples consist of carbonate species as secondary phases due to the adsorption of CO_2 on the powder surface which was transformed to CO_3 during heat treatment. The formation of metal–oxygen (M–O) stretching in the prepared sample is represented by small sharp peak at 732–729 cm^{-1} for all samples. This result is in-agreement with the work by Li et al. [11]. They found that Sr-O, Ba-O, and Nb-O vibration bonding appear between 500–850 cm^{-1} for $Sr_{0.5}Ba_{0.5}NB_2O_6$ powders prepared by aqueous organic gel route using citric acid and EDTA as chelating agents.

In Figure 1b, as calcination temperature increased to 1100 ˚C, the bands associated to the -OH and other organic compounds vibration became weak and disappeared in the IR spectrum. Two absorption peaks appeared at 891-890 indicates that the existance of carbonate residue in C2 and C3. However, no peaks observed for C0 and C1 suggesting that all the carbonate residue was completely decompose during calcination process due to the complete combustion of excessive organic matter with $Ba(NO)_2$. The broad absorption bands between 436 and 442 cm^{-1} indicates the presence of metal oxides, which appeared for all samples.

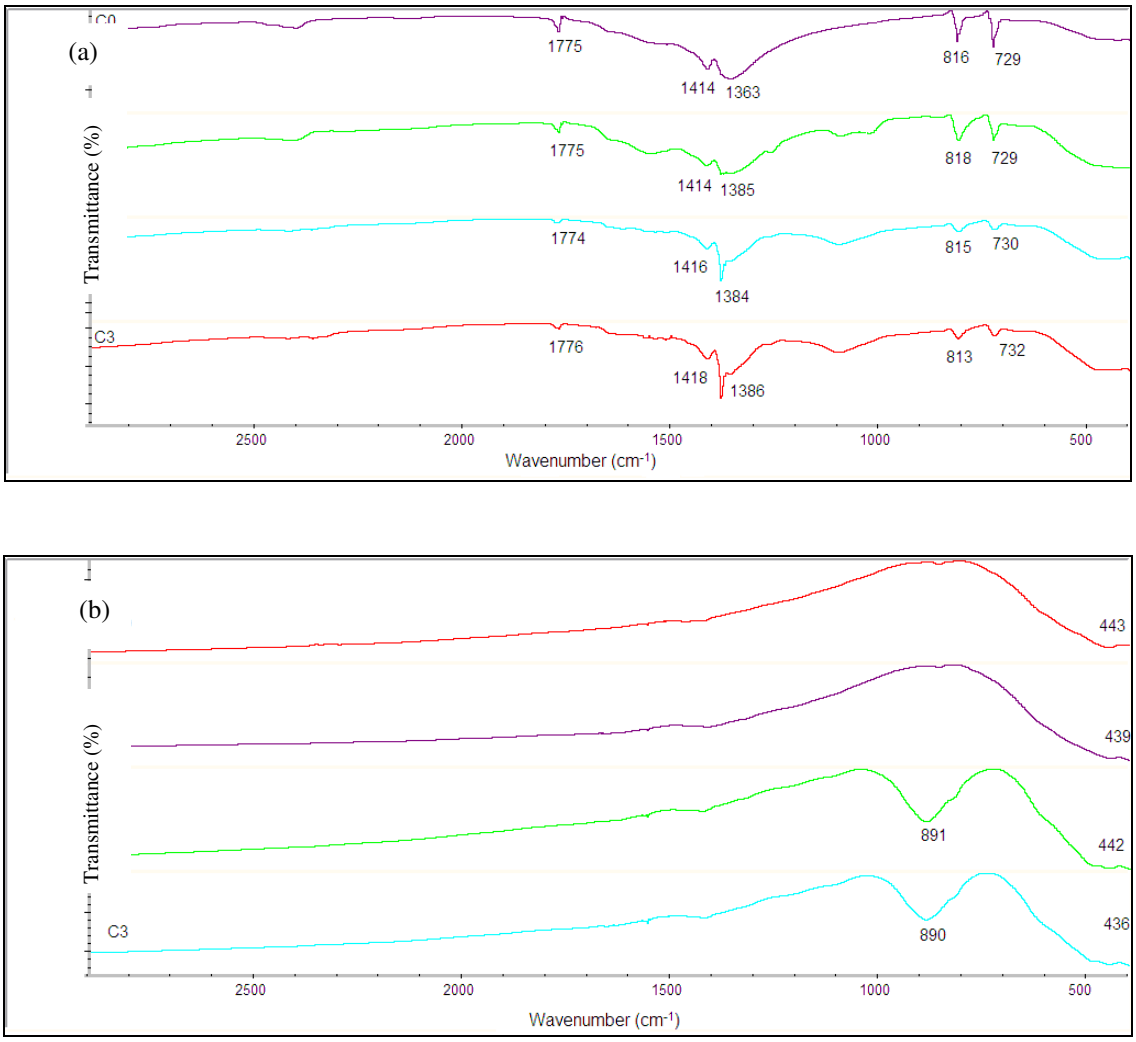

Figure 1: FT-IR spectra of BCY for (a) as-synthesised powder and (b) calcined powder

X-ray diffraction (XRD)

Figure 2 shows X-ray diffraction patterns of BCY sample after calcined at 1100˚C. All calcined powder formed single orthorhombic perovskite phase of $BaCeO_3$ (JCPDS card 822425) [12]. No other significant phases were detected indicating that a complete crystallization of the powder has occurred. Intensity of the peaks in all XRD spectra is decreased as the reaction temperatures increased. The pronounced peaks can be indexed to (211), (022), (231), (213), (040), (422), (611) and (404). However, a small peak due to $BaCO_3$ impurity at $2\theta \approx 26^\circ$ and $2\theta \approx 29^\circ$ was detected in the C2 and C3 samples which was in-agreement with FTIR result as discussed earlier. Table 2 shows a lattice parameter and unit cell volume for the sample treated at different reaction temperatures. C0 and C1 induces an expansion while C2 and C3 induces a contraction in the unit cell volume of $BaCeO_3$ (JCPDS Card-822425).

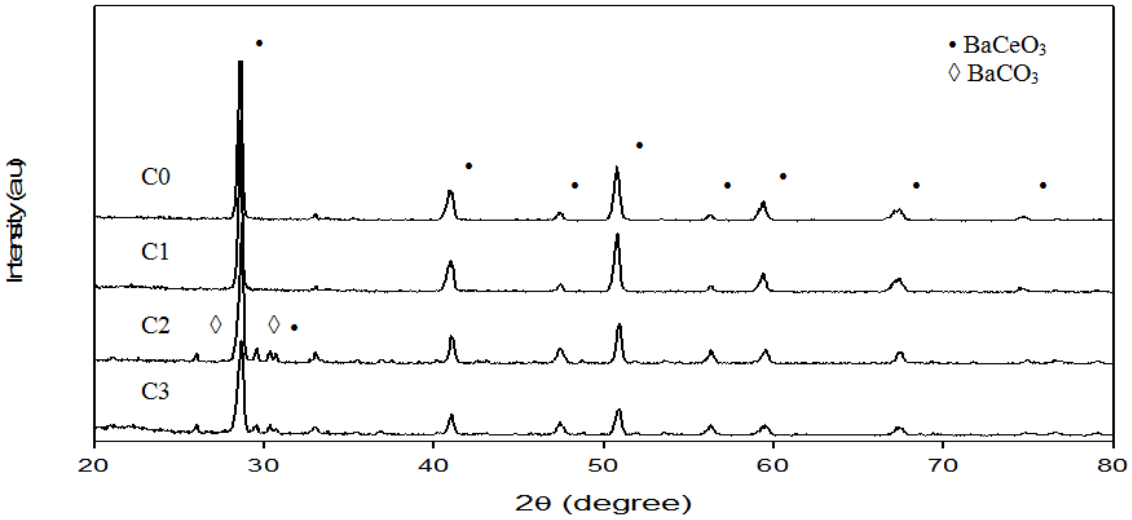

Figure 2 : XRD patterns of the prepared powders after calcined at 1100 ˚C

Table 2: Lattice parameter and unit cell volume of BCY sample

Sample	Lattice Parameter			Unit Cell Volume, V (Å^3)
	a (Å)	b (Å)	c (Å)	
C0	8.768	6.247	6.222	340.802
C1	8.841	6.258	6.201	343.083
C2	8.782	6.217	6.212	339.161
C3	8.655	6.258	6.238	337.869
$BaCeO_3$ (JCPDs card no. 822425)	8.774	6.234	6.214	339.889

CONCLUSION

Sample of BCY was synthesized by a supercritical ethanol using High-Pressure–High-Temperature (HP-HT) Batch Wise Reactor System. At calcination temperature of 1100˚C, a small amount of carbonate impurity still present in the C2 and C3 whereas no such secondary phase was observed for C0 and C1 as proven by FTIR and XRD results. Therefore, we conclude that low reaction temperature during synthesizing process yields better characteristics of BCY ceramic powder compared to high reaction temperature of ethanol.

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