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CHARACTERIZATION OF Y^{3+}-DOPED $BaZrO_3$ SYNTHESIZED USING SUPERCRITICAL ETHANOL AT DIFFERENT REACTION TEMPERATURE

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ABSTRACT

Y^{3+}-doped $BaZrO_3$ (BZY) ceramic powder was prepared by a supercritical fluid method using ethanol as a reaction medium. The respective prepared samples were denoted as Z0, Z1, Z2 and Z3 at four different reaction temperatures with constant (4 MPa) reaction pressure. The formation of metal oxides and carbonate impurity in the samples were analyzed using Fourier transform infrared (FTIR) spectroscopy. The formation of single perovskite phase of BZY sample was identified by X-ray diffractometer (XRD). At 1100 °C, FTIR spectra showed that the carbonate residue still remains in the Z1, Z2 and Z3 samples. However, Z0 free from the carbonate species due to the decomposition of intermediate compounds were completely occurred. The high crystalline single perovskite phase of Z0 was matched to the 'pure' $BaZrO_3$ (JCPDs Card: 060399). It was found that the low reaction temperature of ethanol successful produced highly crystallization of BZY ceramic powder.

Keywords : Supercritical fluids; ceramic perovskite-type oxides; crystalline

INTRODUCTION

Solid oxide fuel cell (SOFC) is a future technology for a highly efficient, fuel flexible, and clean source of energy. The $BaZrO_3$ based material is one of the most promising electrolytes for intermediate temperature SOFC. Doped $BaZrO_3$ (BZY) electrolyte has been recently recognized to exhibit a good chemical and mechanical stability under CO_2 containing atmosphere but its proton conductivity is quite low compared to doped $BaCeO_3$. Y-doped $BaZrO_3$ can be synthesized using the classical solid-state reaction methods that usually need high temperatures about 1400–1700 °C and long annealing duration time (30h). This conventional ceramics powder processing can have several drawbacks such as relatively large and varied grain sizes and inhomogeneities in the chemical composition [1-2].

To overcome these problems, some alternative methods for synthesizing BZY powders have been developed and reported in the literature which are using wet chemical methods such as sol–gel, hydrothermal, co-precipitation, etc. [3–5]. Extensive study on sol-gel method to synthesize BZY powder had gain much more interest from researchers world-wide. However, the major problem is still on the presence of the secondary phases which is $BaCO_3$. Unfortunately, $BaCO_3$ impurities can affect the properties of electroceramics and only a long and tedious washing process using formic acid allows the reduction of the barium carbonate impurity level [6].

Our approach is to improve the characteristic of BZY powders using a supercritical fluid method, with the aim to get single-phase of BZY material at low reaction temperatures. 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 $BaZrO_3$ (BZY) perovskite powder using ethanol as supercritical fluid (SCF) media.

EXPERIMENTAL

Sample preparation.
$Ba(NO_3)_2$(99 %, ACROS), $Zr(NO_3)_2.xH_2O$ (99.5 %,ACROS), and $Y(NO_3)_3.5H_2O$ (99.9 %, Aldrich) were used as starting materials for the preparation of Y^{3+} doped $BaZrO_3$ and ethanol (95 %, HmbG) as reaction medium of solvent [7]. HP-HT batch-wise reactor system is mechanically stirred batch reactor with an internal volume of 350mL. Metal nitrate salt of pre-cursors were dissolved in ethanol inside a vessel. Temperature controller (thermocouple type-K located inside the vessel) and back-pressure regulator (Unijin) were used to control parameters of reaction temperature and pressure as shown in Table 1. The reaction temperature was increased from 150 to 300 °C with 50 °C interval and the reaction pressure was fixed at 4MPa. After 2 hours, the vessel was immediately immersed into cold water to stop the reaction. The sample was collected and transferred into a rotary evaporator to evaporate the remaining solvent. The obtained precipitated was dried at 120 °C and then calcined at 1100 °C with heating rate of 10 °C/min for 6 hours yielding to whitish powder.

Table 1: Denomination of BZY sample at various reaction temperatures with fixed pressure

Denomination of BZY Sample	Reaction Temperature (°C)	Reaction Pressure (MPa)
Z0	150	4
Z1	200	4
Z2	250	4
Z3	300	4

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-Kα radiation (λ = 1.5406 Å) over a 2θ range of 20˚ to 80˚ with step size at 0.02˚/s. The lattice parametes of calcined powders were calculated from the angular positions of the peaks using MathCAD 14 software.

RESULTS AND DISCUSSION

Functional groups analysis.
Figure 1 shows the bonding characteristics of functional groups for the as-synthesised and calcined powders as identified by a FT-IR spectroscopy. The as-synthesised powders (Figure 1a), showed the existing of various organic compounds. A small absorption band around 1632-1620 cm^{-1} for all samples are characteristic of absorbed water or hydroxyl group (O–H stretching) in ethanol. The possible reaction of absorbed water or hydroxyl group is respectively given by equation (1), (2) and (3). The characteristics of metal precursors bound to nitrate group (M-NO_3) for all samples are shown by absorption peaks that appeared at 1485–1484 cm^{-1} and 1371– 1360 cm^{-1} [8]. The presence of a small sharp peak at 810–802 cm^{-1} indicates that the Z1, Z2 and Z3 samples consist of the carbonate species as secondary phases. It suggesting that carbonate ion from the incomplete combustion reacted with $Ba(NO_3)_2$ or Ba^{2+} to form $BaCO_3$ compound.

In Figure 1b, as calcination temperature increased to 1100 ˚C, the bands associated to the -OH and other organic compounds vibration became weaker and disappeared in the IR spectrum. The presence of impurities of nitrate species at 1434-1425 cm^{-1} are still detected in all the spectra [9]. Two absorption peaks appeared at 894-892 cm^{-1} and 995-994 cm^{-1} are related to the characteristic asymmetrical split stretching of carbonate residue in Z1, Z2 and Z3. However, the peaks were not observed for Z0 suggesting that all the carbonate residue was completely decomposed during calcination process. The crystallization of $BaZrO_3$ may expected due to the broad band between 494 and 560 cm^{-1} which are associated to the presence of metal oxide appeared for all samples.

$$\underset{\text{(Ethanol)}}{CH_3CH_2OH(liq)} \longrightarrow \underset{\text{(ethene)}}{CH_2CH_2(gas)} + H_2O(liq) \qquad \text{(Eq. 1)}$$

$$CH_3CH_2OH(liq) + 3O_2(g) \longrightarrow 2CO_2(gas) + 3H_2O(liq) \qquad \text{(Eq. 2)}$$

$$Ba(NO_3)_2(liq) + CH_3CH_2OH(liq) \longrightarrow BA(OH)_2(liq) + CH_3CH_2NO_3(liq) \qquad \text{(Eq. 3)}$$

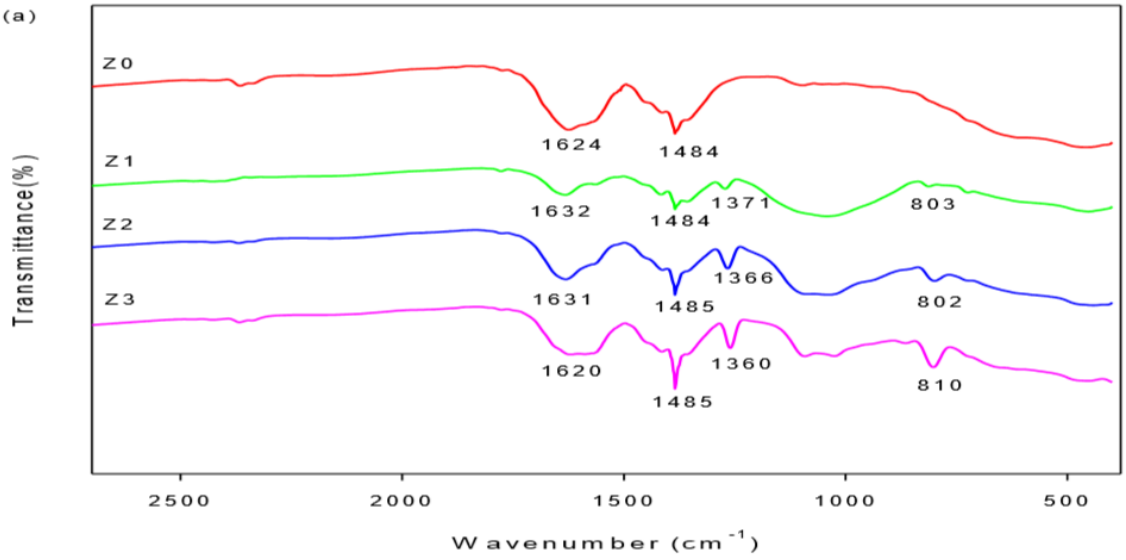

Figure 1(a): FT-IR spectra of BZY for as-synthesised powder

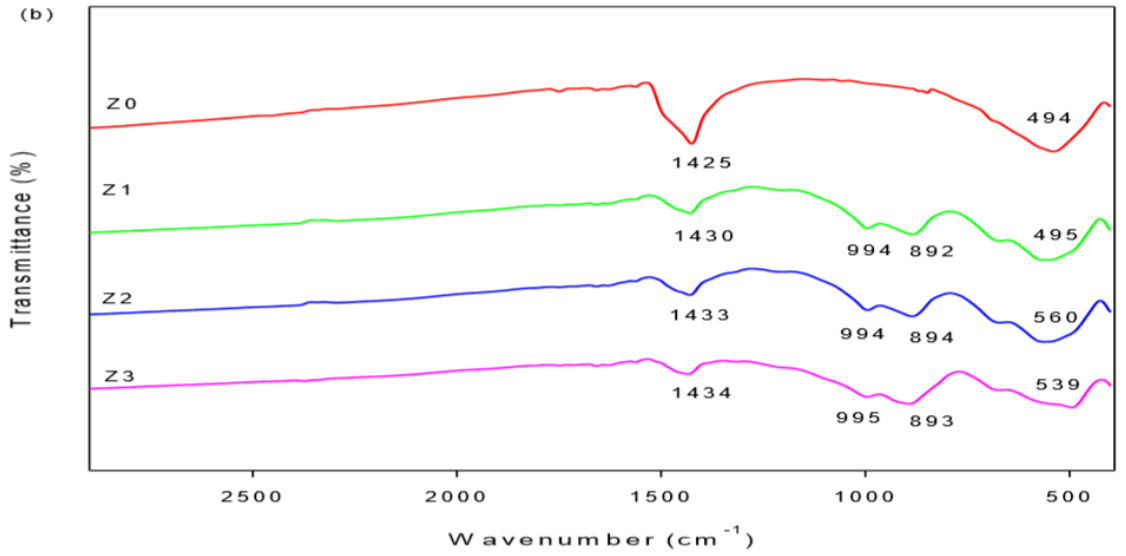

Figure 1(b): FT-IR spectra of BZY for calcined powder

Phase Formation Analysis.

X-ray diffraction patterns of BZY sample after calcined at 1100 °C are shown in Figure 2. The observed diffraction peaks were well matched with JCPDS file of cubic perovskite structure of $BaZrO_3$ (060399). It found that a high crystalline perovskite phase of BZY was obtained at low reaction temperature which are belong to Z0. The

result is in-line with the FTIR results as previously discussed. The pronounced peaks of Z0 can be indexed to (110), (111), (200), (211), (220) and (310). However, samples Z1, Z2 and Z3 exhibited incomplete reaction producing an orthorhombic phase of $BaCO_3$ (JCPDS card 41-0373) were respective detected at 34.9˚, 49.9˚ and 26.05˚. Carbonate compound was formed due to the incomplete combustion of excessive organic matter with $Ba(NO_3)_2$ would generate $BaCO_3$ [10]. The possible reaction is shown in equation (4). Since carbonate compound is stable in air, a high firing temperature as high as 1400°C is needed to eliminate this impurity [11].

$$Ba(NO_3)_2 + CO_2 \longrightarrow BaCO_3 + NO_x \qquad \text{(Eq. 4)}$$

Clearly seen in the table, the different reaction temperature was not significantly changed the unit cell volume. The unit cell volume of Z0, Z1, Z2 and Z3 was respectively about 73.824 $Å^3$, 73.982 $Å^3$, 74.035 $Å^3$ and 74.088 $Å^3$ which slightly increased as compared to pure $BaZrO_3$ (V=73.718 $Å^3$). The small expansion in the unit cell volume may suggest to a complete substitution of Y^{3+} cations at Zr sites but do not considerably change the cubic structure of $BaZrO_3$. A high crystalline of Z0 was formed with 100% percentage of perovskite phase of 'pure' BaZrO3. On the other hand, a crystallinity of the BZY perovskite was reduced since the traces of impurity phase appearred for Z1, Z2 and Z3 samples. A summary of XRD analysis of BZY are presented in Table 2.

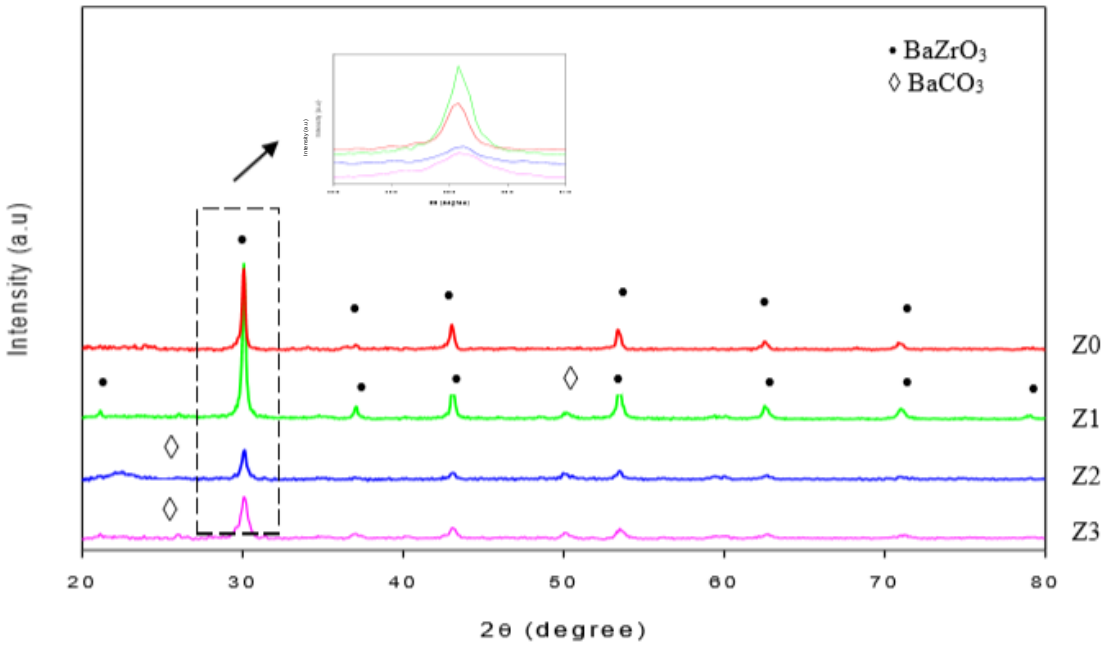

Figure 2 : XRD patterns of the prepared powders after calcined at 1100 °C.

Table 2: Summary of XRD analysis of BZY powders

Sample	Lattice parameter (Å)	Unit Cell Volume V (Å^3)	Percentage of perovskite phase (%)
Z0	4.195	73.824	100
Z1	4.197	73.982	97
Z2	4.199	74.035	87
Z3	4.200	74.088	87
$BaZrO_3$ (JCPDs card no. 060399)	4.193	73.718	-

CONCLUSION

BZY powders were successful synthesised at 150 °C by a supercritical ethanol using High-Pressure– High-Temperature (HP-HT) Batch Wise Reactor System. High crystalline BZY powders were obtained after they were calcined at 1100°C for Z0. However, a small amount of carbonate impurity still present in the Z1, Z2 and Z3 as proven by FTIR and XRD results. Therefore, we conclude that low reaction temperature (Z0) during synthesizing process yields better characteristics of BZY ceramic powder compared to Z1, Z2 and Z3 at high reaction temperature of ethanol.

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