UNIVERSITI TEKNOLOGI MARA

SUPERCRITICAL FLUID: A POTENTIAL ROUTE IN THE SYNTHESIS OF CERATE, ZIRCONATE AND CERATE-ZIRCONATE CERAMICS POWDER

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ABSTRACT

A Supercritical fluid (SCF) is a processing technique which a fluid simultaneously heated and compressed above its critical temperature and pressure. A SCF is used to produce many types of materials since their properties can be varied with different reaction temperature ($T_{reaction}$) and/or reaction pressure ($P_{reaction}$). In this study, cerate and/or zirconate based ceramic powders of $BaCe_{0.9}Y_{0.1}O_{2.95}$ (BCY), $BaZr_{0.9}Y_{0.1}O_{2.95}$ (BZY) and $BaCe_{0.54}Zr_{0.36}Y_{0.1}O_{2.95}$ (BCZY) were synthesized by a high pressure-high temperature (HP-HT) batch wise reactor system using a SCF method. Ethanol was used to synthesize BCY and BZY powders at a constant $P_{reaction}$ (4 MPa) but a different in the $T_{reaction}$ ranging from 150 – 300 °C. Conversely, BCZY powder was synthesized using six different reaction media, namely ethanol, methanol, hexane, pentane, acetone and dichloromethane. Later, a SCF assisted sol-gel (SCF-SG) method was proposed by employment of Polyoxyethyle (10) oleyl ether (Brij97) as a surfactant to improve the properties of BCZY powder. In the synthesis of BCZY sample using a SCF-SG method, a gel was dried at temperature (T_{drying}) of 150 – 325 °C. Then, it was subjected to HP-HT batch wise reactor system using a SCF at a constant $T_{reaction}$ (150 °C) and different $P_{reaction}$ ranging from 2 – 4 MPa. The prepared samples were characterized using Fourier transform infrared (FTIR) spectroscopy, X-ray diffractometry (XRD) and scanning electron microscope/energy dispersive X-ray (SEM/EDX). The presence of carbonate compound at ~800 cm^{-1} and metal-oxide (M–O) bond at 700 – 400 cm^{-1} in the BCY, BZY and BCZY after calcined at 1100 °C was confirmed by FTIR analysis. XRD result revealed that a single perovskite of BCY and BZY was formed at minimum calcination temperature of 800 °C and 1100 °C, respectively. The BCZY prepared by a SCF using ethanol as reaction medium at calcination temperature of 1100 °C showed the less secondary phases of $BaCO_3$, $BaCeO_3$, $BaZrO_3$, CeO_2, ZrO_3, BaO_2 and $Ba(OH)_2$ compared to others medium. The formation of single perovskite phase of BCZY was only obtained after prepared via a SCF-SG at $P_{reaction}$ 2 MPa. The SEM results depicted that the particles of the single perovskite phase of BCY and BZY samples prepared by a SCF are respectively, cubical and spherical in shape. The employment of Brij97 in a SCF-SG produced homogeneous and fewer agglomerated particles with size ranging from 60 to 90 nm. As a conclusion, the used of surfactant in a SCF-SG method able to produce a single perovskite phase of BCZY ceramic powder with homogeneous and fine particles. Therefore, a study on significant parameter involved in a SCF and SCF-SG methods may contribute to a significant new knowledge in the synthesis of cerate, zirconate and cerate-zirconate ceramic powders at a relatively lower processing temperature.

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CHAPTER ONE
INTRODUCTION

1.1 Research Background

Proton conductors are gaining interest due to their potential application as electrolytes in Solid Oxide Fuel Cells (SOFCs), hydrogen separation membranes and hydrogen sensors (Norby, 1999, Park et al., 2014 & Leornadi et al., 2018). One of the proton conductors with larger proton conductivity are ceramics oxides with perovskite related structures with general formula ABO_3 such as $BaZrO_3$, $SrZrO_3$, $SrCeO_3$ and $BaCeO_3$ (A = Ba, Sr; B = Ce, Zr). Among those compounds, doped barium cerate and doped barium zirconate have been widely investigated as a proton conductor. Yttrium-doped barium cerate (BCY) shows the best performance in terms of fuel cell power density at the lower temperatures, but it reacts with CO_2, SO_2 and water vapour to form $BaCO_3$, $BaSO_4$ and $Ba(OH)_2$, respectively (Zhang et al., 2018). On the other hand, Yttrium-doped barium zirconate (BZY) has a good chemical stability under CO_2 containing atmosphere, but shows a lower electrical conductivity than BCY. Furthermore, cerate-zirconates for example $Ba(Ce,Zr)O_3$ have drawn a special attention due to the facts that they exhibit high mechanical stability, high ionic/proton conductivity as well as high chemical stability in carbon dioxide (CO_2) containing atmosphere (Ryu & Haile, 1999). Since then, the countless effort has been made by researchers in order to synthesize this ceramic material using various routes of sample preparation. It is known that the properties of ceramics proton conductor are significantly depending on the synthesis route.

The commonly used method to prepare this ceramics perovskite-type oxide is via a 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. In order to improve the quality of perovskite-type powders for SOFCs application, soft-chemistry routes so-called as the wet chemical methods (WCMs) such as sol-gel, hydrothermal, co-precipitation, etc. have been used to produce the single phase of perovskite at a lower temperature. These chemical