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Phase Formation of $Ba(Ce_{1-x}Zr_x)_{0.90}Y_{0.1}O_{3-\delta}$ Prepared by a Modified Sol-Gel Method

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Abstract—The powders of $Ba(Ce_{1-x}Zr_x)_{0.90}Y_{0.1}O_{3-\delta}$ (BCZY) with $0.2 \leq x \leq 0.6$ have been prepared by a modified sol-gel method. Triethylenetetramine (TETA) was employed as chelating agent. Phase formation of calcined powders at 1100°C and sintered pellets at 1400°C of BCZY were examined by an X-ray diffractrometer (XRD). XRD results showed the calcined powder and sintered pellet formed a single perovskite phase over the entire range of x values. As the amount of zirconium substitution (x values) increase, the main peaks are shifted to the higher 2theta values which suggest a complete substitution of zirconium into cerium sites. All the obtained calcined powders and sintered pellets possess cubic structure (Pm-3m) at all x values.

***Keywords*—**Structure, phase formation, modified sol-gel, cerate-zirconate electrolye, XRD.

I. INTRODUCTION

A lot of researches have been conducted to improve the performance of cathode, anode and electrolyte for electrochemical devices such as fuel cell. The researches toward electrolyte are widely developed world wide. Nowadays, researches are focused on producing cerate-zirconate material to enhance the properties of electrolyte in terms of mechanical and chemical stability. It is well known that barium cerate has some of the highest protonic conductivity of the other oxide examined. On the other hand, barium zirconate have superior chemical and mechanical strength but this material provides lower conductivity value. Chemical and mechanical stability are two major aspects that contributed to the performance of fuel cell system. Ryu et al. [1] and Katahira et al. [2] reported that better chemical stability obtained by partial substitution of Zr^{+4} cations into Ce^{+4} cations. However, the structure also plays an important role in the properties of an electrolyte. Bae et al. [3] reported that $Ba(Ce_{0.8}Zr_{0.2})O_3$ powders formed orthorhombic structure with the space group of *Imma*. The structure of orthorhombic also was obtained by Osman et al. [4] in their study. But, according to Wienstroer et al. the structure of $BaCe_{0.9-x}Zr_xNd_{0.1}O_{3-\delta}$ ($0.1 \leq x \leq 0.9$) is cubic with space group of pm-3m. These inconsistencies are attractive to be confirmed. Since the performances of an electrolyte are measured by the value of its conductivity, doping was often used to enhance the conductivity value. According to Iwahara *et al.*, perovskites based on cerate-zirconate showed protonic conducting behavior when doped with trivalent or divalent cations such as yttrium or ytterbium. Since structure also influences the mechanical properties, several researches on Zr substitution into cerate site have been reported [5]-[10]. However, this study will focus only on the structure of $Ba(Ce_{1-x}Zr_x)_{0.90}Y_{0.1}O_{3-\delta}$ ($0.2 \leq x \leq 0.6$).

II. EXPERIMENTAL

A compound of $Ba(Ce_{1-x}Zr_x)_{0.90}Y_{0.1}O_{3-\delta}$ was synthesized by a modified sol-gel method with metal- nitrate salts as starting material. Stoichiometric amounts of Barium nitrate (Acros, 99%), Cerium(III) nitrate hexahydrate (Acros, 99.5%), Zirconyl (IV) nitrate hydrate (Acros, 99.5%) and Yttrium (III) nitrate hexahydrate (Acros, 99.9%) were dissolved in deionized water until transparent nitrate solution is formed. Triethylenetetramine (TETA) was added as chelating agent followed by ethylene glycol to form metal-complex solution. The value of pH has been controlled to 11. The resulting solution was heated at 120°C by using a hot plate until the solution became turned into gel form and changed to brownish color. During this stage of heat treatment, the NO_x gaseous were released. Then, the temperature was increased gradually to 325°C for 12 hours to transform the samples into black hard sponge-like. Then, the samples were pre-calcined at 550°C for 2 hours and 1100°C for 10 hours to ensure all of the organic compounds were eliminated. After this calcination process, the yellowish powder has been produced. The powders obtained were characterized by using PANalytical's X-ray diffractometers.

The calcined powders were pressed into pellet form with diameter and thickness of 13 mm and 1 mm, respectively. The geometrical density of green pellet was calculated before the pellets were sintered at 1400°C in air for 10 hours. The geometrical density for sintered pellet was also calculated. Then, the phases of the samples were characterized using XRD.

All of the samples were characterized by using X-ray diffraction (XRD) PAN Alytical X'pert Pro MPD (CuK_α, λ=1.5406Å) from 20° to 80° with scan rates of 5^0/min at room temperature. In order to confirm the space group, the Rietveld refinement was executed.

III. RESULTS AND DISCUSSION

Fig. 1 shows the XRD spectra of $Ba(Ce_{1-x}Zr_x)_{0.9}Y_{0.1}O_{2.95}$ ($0.2 \leq x \leq 0.6$) at calcination temperature of 1100°C. The

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profiles obtained at entire range of *x* shows single perovskite phase. For all composition, a cubic perovskite structure was found. The spectra show that the major peaks are shifted to the higher value of 2 Theta. The diffraction peaks are broader as the amount of zirconium substitutions decreases. The width of a diffraction peak is also influenced by the crystallite size. A large crystallite size causes sharp reflections, whereas a small size leads to broad reflections.

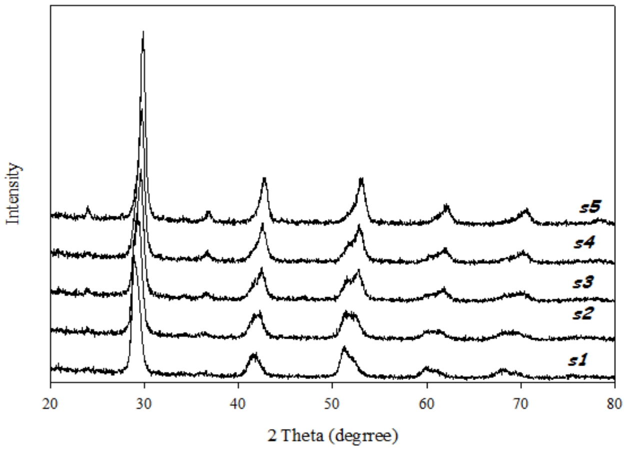

Fig. 1 XRD spectra of $Ba(Ce_{1-x}Zr_x)_{0.90}Y_{0.1}O_{3-\delta}$ powders after calcined at 1100ºC

Fig. 2 shows the XRD spectra for the sintered pellets. The profiles obtained at entire range of *x* also show the single perovskite phase. As the value of *x* increase, the main peaks of the XRD spectra are shifted to the higher angle of 2theta values which suggest a complete substitution of zirconium into cerium sites. The cubic structure was obtained for the entire range of *x*. This result was supported by Wienstroer et al. [7] in their study. The reference diffraction pattern by the Joint Committee on Powder Diffraction Standard, (JCPDS) was used to determine the perovskite phase. The reference card of 98-005-6812 was used for sample 1, 98-004-8576 was used for sample 2 and 3, and 98-005-6805 was used for sample 4 and 5 to compare the spectra. The space group for each sample was revealed by using the Rietveld refinement and shows that all samples are in the same space group pm-3m.

Table I shows the Lattice parameters and unit cell volume of $Ba(Ce_{1-x}Zr_x)_{0.9}Y_{0.1}O_{3-\delta}$ $(0.2 \leq x \leq 0.6)$. The value of unit cell volume is gradually decreased as the value of *x* increased. The relative density for each sample also have been calculated and tabulated in Table II. The highest relative density was obtained at *x*= 0.2 (98.8%) and the lowest relative density obtained at *x* = 0.6 (85.6 %). Small grained powders can result in sintered pellet with high density, small voids and grains, which lead to a high ionic conductivity. The value of relative density varies depending on the composition of Zr and relative density of the samples decrease as the composition of Zr increase.

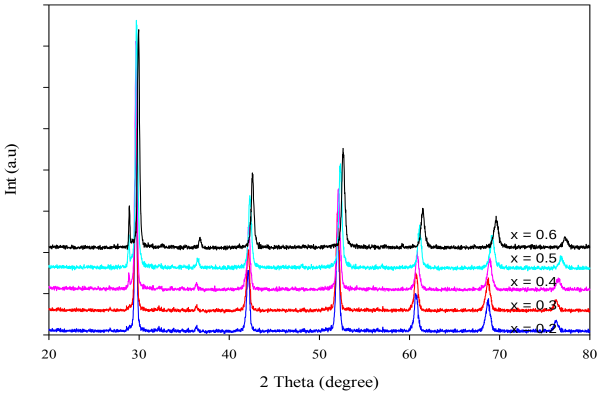

Fig. 2 XRD spectra for $Ba(Ce_{1-x}Zr_x)_{0.90}Y_{0.1}O_{3-\delta}$ pellets after sintered at 1400ºC

TABLE I
LATTICE PARAMETERS AND UNIT CELL VOLUME OF $BA(CE_{1-X}ZR_X)_{0.90}Y_{0\cdot1}O_{3-\Delta}$

x	a (Å)	unit cell volume (Å)
0.2	4.37	83.53
0.3	4.36	82.92
0.4	4.34	81.78
0.5	4.32	80.66
0.6	4.30	79.70

TABLE II
RELATIVE DENSITY OF $Ba(Ce_{1-X}Zr_x)_{0.90}Y_{0\cdot1}O_{3-\delta}$

x	Geometrical density (g/cm^3)	XRD density (g/cm^3)	Relative density (%)
0.2	6.19	6.27	98
0.3	5.79	6.31	91
0.4	5.74	6.40	89
0.5	5.57	6.40	87
0.6	5.28	6.17	85

In order to confirm the substitutions of Zirconium into Cerium sites has successfully occurred, the graph of Lattice parameter versus Zr substitutions were plotted (Fig. 3). A linear straight line should be formed to show the substitutions progress. As reported by Osman et al., the contraction of unit cell volume of the samples suggested a complete substitution of zirconium into cerium sites [11]. Fig. 3 shows that a linear straight line was formed and confirmed that the substitutions of Zirconium into Cerium sites was successfully occurred.

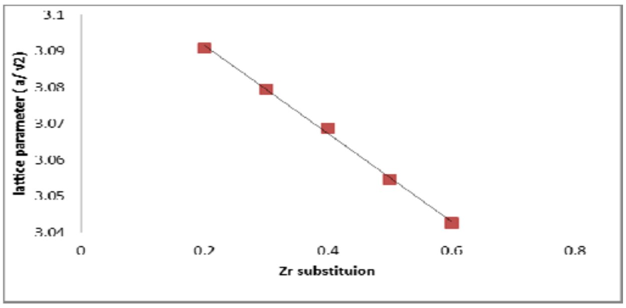

Fig. 3 Lattice parameter versus Zr substitutions

IV. CONCLUSION

Single-phase perovskite of $Ba(Ce_{1-x}Zr_x)_{0.9}Y_{0.1}O_{3-\delta}$ $(0.2 \le x \le 0.6)$ was successfully prepared by using a modified sol gel method. The XRD analysis was revealed that a cubic perovskite structure with space group of pm-3m was formed for entire range of x values. The unit cell volume and relative density of the samples decrease as amount of Zr substitutions increased. The substitutions of Zirconium into Cerium site were successfully occurred.

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