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## The Synthesis and Characterizations of CeY<sub>0.15</sub>Er<sub>0.05</sub>O<sub>2</sub> Nanocrystal

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CeY<sub>0.15</sub>Er<sub>0.05</sub>O<sub>2</sub> nanocrystal powders prepared via sol-gel method. Phases identification have been made X-ray diffraction, SEM-EDX, FTIR, thermal and impedance analysis. XRD data show that all powders were obtained with cubic fluorite structure. With the increase of sintering temperature, the unit cell size decreased and the crystal size increased. The particle size was found to be in the range of 150 to 270 nm. It was found that the nitrates and organic species seen in the FTIR results. It was observed that organic species disappeared at sintering temperatures selected according to thermal analysis results. Impedance measurements of the pelletized sample were made. Although the crystal structure properties were good, it was found that the conductivity values were low.

**Keywords:** Co-doping, ceramic electrolyte, SOFC.

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### Introduction

The search for alternative energy has attracted attention recently due to the depletion of fossil energy resources and the influence of greenhouse gases. Studies on the solid oxide fuel cells is increasing due to their properties such as lower greenhouse gas emissions and high efficiency [1, 2]. Solid oxide fuel cells are systems that convert chemical energy directly into electrical energy [3]. It simply consists of an anode, a cathode electrode and an electrolyte. The most important component of a solid oxide fuel cell is the electrolyte. The electrolyte must have oxygen ionic conductivity, be stable and not react chemically with other components [4, 5]. 8YSZ is the most well-known and studied electrolyte. However, it shows high oxygen conductivity above 1273 K. This increase in temperature causes the cost and degradation of other components of the fuel cell. As an alternative to ZrO<sub>2</sub>-based electrolytes, CeO<sub>2</sub> electrolytes exhibit oxygen ionic conductivity with their fluorite- crystal structure. And it can reduce the working temperature to 823 - 1073 K. Increasing of the conductivity of CeO<sub>2</sub> electrolytes are depend on type of doped, amount of doped, doped ionic radius, synthesis conditions [4, 5 - 9].

Until now, different compounds and different amount ratio doped in CeO<sub>2</sub> have been studied. It has been found that the high conductivity of Gd and Sm [10-14]. However, it has been observed recently that the co-doping improves the conductivity by 10 - 15 % according to the single doping [14 - 16]. When synthesis CeO<sub>2</sub> ceramic electrolytes, it has been found that the dope range should be within the range of 1 - 20 %, and high ratios decrease the conductivity value [17]. Ions with a radius more than Ce are increased that conductivity because increase vacancy ratio of oxygen mobile. In addition, the nanoparticle size in the synthesis process has a positive effect on the conductivity to increase the surface area. For this, hydrothermal, sol- gel, glycine nitrate, pechini, solid state-ball milling are used in synthesis processes [18, 19].

In this study, Y<sup>3+</sup> and Er<sup>3+</sup> co-doped ceria based material was prepared via sol-gel method. The crystalline, thermal, microstructural and electrical properties of the obtained compounds were detailed investigated.

## I. Material and method

The powder electrolytes of  $\text{CeY}_{0.15}\text{Er}_{0.05}\text{O}_2$  was synthesized via sol-gel method. Cerium (III) nitrate hexahydrate  $[\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}]$  (pure 99,99 %, Alfa Aesar), erbium(III)nitrate pentahydrate  $[\text{Er}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}]$  (pure 99,9 %, Arcos organics) and yttrium(III)nitrate hexahydrate  $[\text{Y}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}]$  (pure 99,9 %, Arcos organics) were used as a preparation materials. The stoichiometric amounts of cerium, yttrium and erbium nitrates were dissolved in ultrapure water. Citric acid was slowly added to the transparent solution during mixing on the magnetic stirrer. Citric acid was completely dissolved and then ethylene glycol was added. After then, this solution heated to 353 - 363 K and heating continued until the gel was formed and this transparent solution was converted to before yellow and then orange after about 3 hours. Stirring was not done during the heating. The orange gel was heated in the air and dried at 393 K for 18 hours. Then, the dried mixtures were ground in an agate mortar. The powder samples applied a heat treatment in an alumina crucible at 873, 1073, 1273 K for 48h respectively.

The crystal structures parameters of all prepared electrolyte were characterized a Pan analytical Empryan X- ray diffractometer with  $\text{Cu K}\alpha_1$  (1.5406 Å) radiation. The XRD spectra were obtained 0.1 deg/s scan rate,  $0.013^\circ$  step size and  $10 - 90^\circ$   $2\theta$  range. The crystallite size were calculated from using Scherrer equation of X'Pert High Score Plus software. The morphology of samples was determined by using a Zeiss EVO 10LS scanning electron microscopy. The thermogravimetric and differential thermal analysis were perform SEIKO

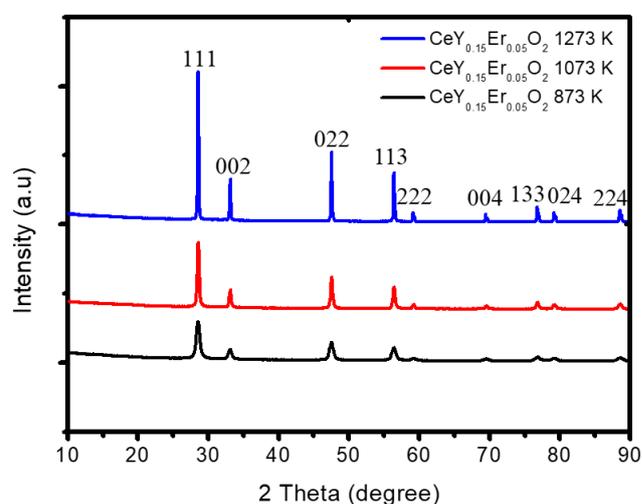
Exstar TG-DTA system. The heating rate, gas flow and temperature range are 10K/min, 200 mL/min and 323K – 1473 K, respectively. The FTIR absorption spectra were recorded at room temperature in the wave number range of  $4000 - 400 \text{ cm}^{-1}$  using a Perkin-Elmer Frontier FTIR spectrometer with ATR technique which have a resolution of  $4 \text{ cm}^{-1}$ .

The sample was disk-shaped for investigated the sample of electrical properties. Disk shaped sample was sintered at 1473 K for 6h. Before the resistance measurements, both surface of pellet was painted with silver paste. The electrical properties of material were studied using electrochemical two probe impedance spectroscopy. The electrochemical impedance

measurement was performed with Solartron 1260 (Farnborough, UK). The electrochemical Impedance Spectra (EIS) were recorded in the frequency range of 0.01 Hz - 13 MHz and applied bias voltage with and amplitude of 100 mV AC. Impedance measurement was performed varying the temperature from 473 K to 973 K in air atmosphere.

## II. Result and Discussion

The XRD pattern of the Ce based Y and Er co-doped samples are shown in Fig. 1. The all prepared samples diffraction peaks appeared at  $2\theta$  of  $28.48^\circ$ ,  $33.01^\circ$ ,  $47.37^\circ$ ,  $56.20^\circ$ ,  $58.94^\circ$ ,  $69.23^\circ$ ,  $76.49^\circ$ ,  $78.86^\circ$  and  $88.17^\circ$  were respectively indexed to the (111), (002), (022), (113), (222), (004), (133), (024) and (224) phase of single-phase face centered cubic  $\text{CeO}_2$  (Ia-3d) structure. These patterns are in a good agreement with the pattern (ICSD 98-015-5608).



**Fig. 1.** XRD patterns of  $\text{CeY}_{0.15}\text{Er}_{0.05}\text{O}_2$  samples at different temperatures.

The unit cell parameters of all samples (Er and Y co-doped  $\text{CeO}_2$ ) are shown in Table 1. The narrow spectral width characteristic peaks indicated that the products were high crystalline degree. The crystalline size Er and Y co-doped  $\text{CeO}_2$  are calculated according to the Debye-Scherrer equations (Eq.1). The using the sharpest diffraction peaks (111, 022, and 113) was performed the crystalline size calculation.

**Table 1**

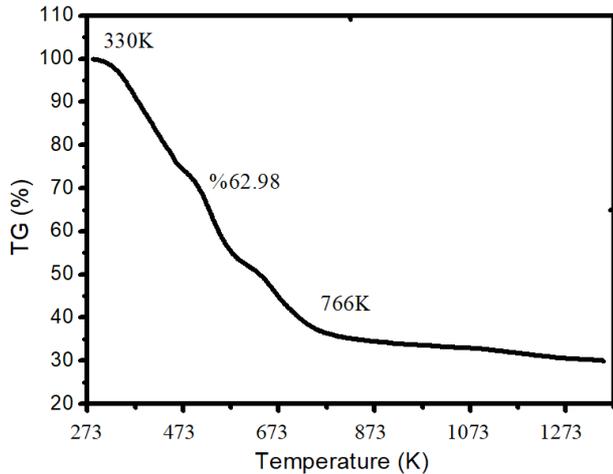
The unit cell parameters of all prepared samples

Samples	Lattice parameters	Space Group	Volume	Crystalline size (nm)			
				Mean value	(111)	(022)	(113)
$\text{CeY}_{0.15}\text{Er}_{0.05}\text{O}_2$ (873 K)	5.4091	Ia-3d	$(\text{Å})^3$ 158.25	14.38	15.47	13.30	15.83
$\text{CeY}_{0.15}\text{Er}_{0.05}\text{O}_2$ (1073 K)	5.4079	Ia-3d	158.16	38.20	40.45	38.85	34.16
$\text{CeY}_{0.15}\text{Er}_{0.05}\text{O}_2$ (1273 K)	5.4076	Ia-3d	158.14	147.27	143.62	152.28	147.73

$$D = \frac{0.89 \lambda}{\beta \cos \theta} \quad \beta = \beta_{obs} - \beta_{std} \quad (1)$$

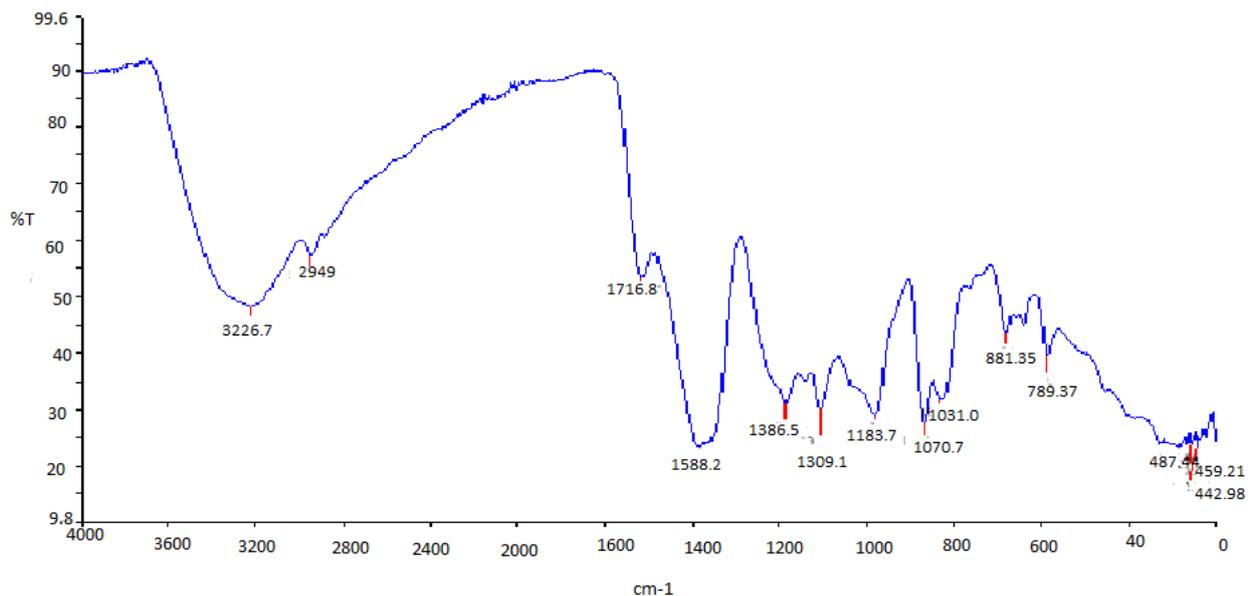
where D crystalline size,  $\lambda$  is the X-ray wavelength angular line,  $\beta$  full width at half maximum (FWHM) and  $\theta$  the Bragg's angle. As the sintering temperature increased, the XRD peaks shaper point out the improved crystallinity.

The TG curves of results were shown in Fig. 2 The loss of total mass from 6.350 mg to 2.350 mg, seen between 330 K and 766 K. According to TG, surface water of precursor powders, nitrates, molecular water, ethylene glycol and citric acid separation in the synthesis lead to mass loss. 773K, there is no mass loss after decomposition of organic species.



**Fig. 2.** TG curves of CeY<sub>0.05</sub>Er<sub>0.15</sub>O<sub>2</sub> gel precursor.

Gel precursors were used for FT-IR analysis. Fig. 3 shows the spectrum of gel precursor sample. According to the spectrum results, citric acid and ethylene glycol are contained in the sample. These exhibited bands regions. The bands indicate stretching in the region 789.37 cm<sup>-1</sup> Ce-O and 1000 - 1700 cm<sup>-1</sup> un-decomposed nitrates



**Fig. 3.** FT-IR spectra of gel precursor.

precursor. The 3226.7 cm<sup>-1</sup> of band is -OH stretching originated from ethylene glycol and citric acid.

The Er and Y co-doped lower total conductivity as it has been observed in some recent literatures. One of the reasons for this is critical dopant ionic radius. Other reason possibly due to the erbium oxide, contributing to the higher resistivity [20]. It has been observed that the conductivity of the doped type whose ionic radius is lower than Ce is lowered. The work of Omer et.al shown that the effect of the radius of impurity on the conductivity [21]. In this study the graph compares the effect on ionic radius of trivalent different dopant cation with pure CeO<sub>2</sub>. Ionic radius for Er<sup>3+</sup> 1.004 Å, and Y<sup>3+</sup> 1.019 Å, Ce<sup>4+</sup>, 0.97 Å, Ce<sup>3+</sup> 1.143 Å. The ionic radius decreases the unit cell parameter and this restricts the oxygen mobility in crystals structure.

## Conclusions

CeY<sub>0.15</sub>Er<sub>0.05</sub>O<sub>2</sub> ternary compounds were synthesized by the sol-gel method. The cubic fluorite structure of CeO<sub>2</sub> was obtained in the three different molar ratios. The single phase samples were observed to have their grain dimensions changed between 150 - 270 nm. Porous structure between particles is caused in poor bonding to low conductivity. The Er<sup>3+</sup> used for the single- phase ceramic electrolyte was affects the negative for the ionic conductivity of ceria-based electrolytes.

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- [1] E. Bompard R. Napoli, B. Wan, G. Orsello International Journal of Hydrogen Energy 33(12), 3243 (2008); <https://doi.org/10.1016/j.ijhydene.2008.04.017>.
- [2] J.P.P. Huijsmans, F.P.F. Van Berkel, G.M. Christie, Journal of Power Sources 71(1), 107 (1998); [https://doi.org/10.1016/S0378-7753\(97\)02789-4](https://doi.org/10.1016/S0378-7753(97)02789-4).
- [3] F.M.L. Figueiredo, F.M.B Marques, Wiley Interdisciplinary Reviews: Energy and Environment 2(1), 52 (2013); <https://doi.org/10.1002/wene.23>.
- [4] N. Mahato, A. Banerjee, A. Gupta, S. Omar, K. Balani, Progress in Materials Science 72, 141(2015); <https://doi.org/10.1016/j.pmatsci.2015.01.001>.
- [5] T. Mori, J. Drennan Journal of electroceramics 17(2-4), 749 (2012); <https://doi.org/10.14723/tmrsj.20thAnniv.5>.
- [6] S.Y. Gómez, D. Hotza Renewable and Sustainable Energy Reviews 61, 155 (2016); <https://doi.org/10.1016/j.rser.2016.03.005>.
- [7] L. Malavasi, C.A. Fisher, Chemical Society Reviews 39(11), 4370 (2010); <https://doi.org/10.1039/B915141A>.
- [8] J.B. Goodenough Annual review of materials research 33(1), 91 (2003); <https://doi.org/10.1146/annurev.matsci.33.022802.091651>.
- [9] Li B., X. Wei, W. Pan, International journal of hydrogen energy 35(7), 3018 (2010); <https://doi.org/10.1016/j.ijhydene.2009.07.002>.
- [10] W. Zając, J. Molenda, Solid State Ionics 179(1-6), 154 (2008); <https://doi.org/10.1016/j.ssi.2007.12.047>.
- [11] O. Mendiuk, M. Nawrocki, L. Kepinski, Ceramics International 42(1), 1998 (2016); <https://doi.org/10.1016/j.ceramint.2015.10.006>.
- [12] M.R. Cesário, E. Savary, S. Marinel, B. Raveau, V. Caignaert, Solid State Ionics 294, 67 (2016); <https://doi.org/10.1016/j.ssi.2016.07.005>.
- [13] B.C.H. Steele, Solid state ionics 129(1), 95 (2000); [https://doi.org/10.1016/S0167-2738\(99\)00319-7](https://doi.org/10.1016/S0167-2738(99)00319-7).
- [14] S.K. Tadokoro, E.N.S. Muccillo, Journal of the European Ceramic Society 27(13-15), 4261 (2007); <https://doi.org/10.1016/j.jeurceramsoc.2007.02.138>.
- [15] K. Tanwar, N. Jaiswal, D. Kumar, O. Parkash, Journal of Alloys and Compounds 684, 683 (2016); <https://doi.org/10.1016/j.jallcom.2016.05.223>.
- [16] K.C. Anjaneya, G.P. Nayaka, J. Manjanna, G. Govindaraj, K.N. Ganesha, Journal of Alloys and Compounds 578, 53 (2013); <https://doi.org/10.1016/j.jallcom.2013.05.010>.
- [17] C.C. Chou, C.F. Huang, T.H. Yeh, Ceramics International 39, 627 (2013); <https://doi.org/10.1016/j.ceramint.2012.10.150>.
- [18] G. Kim, N. Lee, K.B. Kim, B.K. Kim, H. Chang, S.J. Song, J.Y. Park, International Journal of Hydrogen Energy 38(3), 1571 (2013); <https://doi.org/10.1016/j.ijhydene.2012.11.044>.
- [19] J. Brinker, Sol-Gel Science The physics and chemistry of sol-gel processing (NewYork, Academic Press, 1990).
- [20] S. Kuharuangrong, Journal of Power Sources 171(2), 506 (2007); <https://doi.org/10.1016/j.jpowsour.2007.05.104>.
- [21] S. Omar, E.D. Wachsman, J.L. Jones, J.C., Journal of the American Ceramic Society 92(11), 2674 (2009). <https://doi.org/10.1111/j.1551-2916.2009.03273.x>.

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## Синтез та характеристики нанокристалів $\text{CeY}_{0.15}\text{Er}_{0.05}\text{O}_2$

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Нанокристалічні порошки  $\text{CeY}_{0.15}\text{Er}_{0.05}\text{O}_2$  отримано золь-гель методом. Методом рентгенівської дифракції виконано ідентифікацію фаз, проведено SEM-EDX, FTIR, а також термічний та імпедансний аналізи. Дані XRD показують, що всі отримані порошки володіли кубічною структурою флюориту. Зі збільшенням температури спікання розмір елементарної комірки зменшувався, а розмір кристалів збільшувався. Встановлено, що розмір частинок знаходився в діапазоні від 150 до 270 нм. Встановлено, що спостерігаються нітрати та органічні включення, які виявлені із FTIR. Було помічено, що органічні включення зникали при температурах спікання, вибраних за результатами термічного аналізу. Виконано вимірювання імпедансу гранульованого зразка. Хоча властивості кристалічної структури були хорошими, отримані значення провідності були низькими.

**Ключові слова:** легування, керамічний електроліт, SOFC.