Conductivity studies on mechanically alloyed Nano-CSZ powders

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Abstract:

9 mol%, 12mol% and 15mol% Calcia is mixed with commercial micron sized zirconia Powder mechanically in ball milling under cryogenic conditions to get nano sized powders. Powders were checked for development of stabilised structures and electrical conductivity studies were performed on Nano-CSZ pellets sintered at 1600°C for 2 hr. Samples were tested for AC conductivity and dielectric constant using 2 probe method. AC conductivity is found to increase with temperature. dielectric constant decreased exponentially with frequency at all temperatures. Electrical properties of Low cost Nano CSZ powder produced mechanically is suitable for SOFC applications.

Keywords. Calcia stabilised zirconia, Sintering, Ball milling, Conductivity, dielectric constant, Electrical properties, CSZ. CSZ- Calcia Stabilised Zirconia, SOFC-Solid Oxide Fuel Cell

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1. INTRODUCTION

At normal temperature, pure zirconium dioxide has a monoclinic crystal structure but when the temperature rises from room temperature to the melting point, its structure changes from tetragonal to cubic.During the phase transition from cubic to tetragonal to monoclinic large stresses are created causing purer zirconium dioxide to break when cooled causing unstability to retain structure. Various oxides of Magnesia, yttria, calcia or ceria in variable proportions are added to stabilise the tetragonal and or cubic phases.The tetragonal phase in zirconia can be metastable in some instances, and if enough of this metastable phase is present, the tetragonal phase can change to monoclinic phase, causing volume expansion. The toughening due to transformation increases reliability and durability.

The stabilised zirconia ceramics are utilized to determine oxygen content in gases,exhaust gases and in solid oxide fuel cells [1] as it has high oxygen conductivity. They've long been applied as a sensor to boost combustion efficiency. Since fully stabilised zirconia is easily affected by thermal shock and it is a concern in electrochemical cells, hence partially stabilized zirconia (PSZ) cells is preferred. Because of great strength and fracture toughness, stabilized zirconia have vital engineering applications in fuel cells [2].

But researchers have invested time and efforts to produce low cost stabilized zirconia powder by adopting various routes and techniques and at under various processing conditions. Methods like, Sol-gel [4], spray pyrolysis [5-6], precipitation routes [7], and rapid combustion routes [8,9] are the most effective techniques for synthesis of CSZ powders with high purity. From the various routes of obtaining CSZ powders[10],mechanical alloying is used for cost effectiveness with little compromise on properties. The sintering of different mol fraction zirconia powders at different temperatures are studied for different properties by researchers[11-16].The present

work deals with knowing the effects of high temperature sintering at 1600°C for 2 hours on microstructure and conductivity behaviors of nano-CSZ powders obtained from mechanical means for SOFC applications.

2. MAIN TEXT

2.1 EXPERIMENTAL WORK

Commercial Powders of 10 micron size CaO and five micron sized Zirconia were procured from sigma Aldrich. Three compositions by molar weight percentage of 9 %,12 % 15 % CaO were prepared with zirconia as matrix. Powder mixtures were weighed and loaded on to planetary ball mill in zirconium steel jars of 500mL with liquid nitrogen and grinding media. 40 Zirconium steel balls of 15gm each with mass ratio of steel ball to powder of 10:1 is employed. Jars with occupied volume as1/3of total volume were run for 80hrs with short gap at300rpm. The milled samples were analysed in the 2-θ range 20º-80º at a speed of 1° per minute utilising X-ray Diffraction techniques with CuKα radiation (D8-Advance). Scanning electron microscopy (SEM) to investigate the powder sample (SEM; Quanta 200 FEG, FEI). To prepare green pellets about 20 g of the powder obtained after milling of each compositions separately is mixed with 3 wt% binding agent, polyvinyl alcohol and compacted under uniaxial press using a suitable cylindrical die. Within the cylindrical die, stearic acid was used as a lubricant, and a compaction pressure of 13 tonnes was used. Green pellets are sintered in a muffle furnace at 1600°C for 2 hours at a rate of 5 °C/min heating and cooling. Furthermore, the sample was withdrawn from the furnace after it had been allowed to cool naturally for 24 hours.

SEM is used to know the grain size and surface characteristics of pellets post sintering. Grain size influences conductivity and hence SEM is carried out by coating with gold as the system is non-conducting at room temperature. Both the surfaces of sintered cylindrical pellets were polished using abrasive paper. Silver paste is applied on both sides and pellets are thermally treated at 150 ºC for half an hour with a heating rate of 3ºC/min. AC conductivity and the dielectric constant of the treated pellets were studied at temperature range 300-500°C using an 2 probe sample holder with a tube furnace (HIOKI 3532 – LCR) in the range of 100 -10^6 Hz frequency.

2.2 RESULTS AND DISCUSSION

Figure 2.1 illustrates the XRD patterns of Calcia stabilised zirconia (CSZ) powders with diffraction peaks reveals the presence of cubic and tetragonal zirconia. The data from the Joint Committee on Powder Diffraction Standards is compared to all peaks derived by XRD analysis (JCPDS). Using Scherrer formula, average grain size, $D = (0.9\lambda) / (\beta \cos\theta)$ was calculated where in the formulae, λ is the X-ray wavelength(0.154nm) of CuKα radiation. θ is Bragg angle, and β = Full Width Half Maxima of the XRD peak appearing at the Bragg's diffraction angle θ. 21nm was the grain size average found from XRD studies.

SEM studies reveals that, the particles are in uniform and spherical shape with nano-particles size distribution, narrow, as shown in Figure 2.2. It also confirms that morphology is good with nanoparticles of similar smaller sizes. Some tendency of agglomeration is observed but to a lesser extent and particles are uniform in shape and size. The EDS spectrum (Figure 2.3) reveals that content and purity of the powder samples synthesized under cryogenic condition are good. The TEM micrograph of synthesized Nano-CSZ powder (Calcia Stabilized Zirconia) powder, shown in Figure 2.4,which indicates that the particles are mostly spherical and uniform in size with a particle size average of approximately 30 nm.

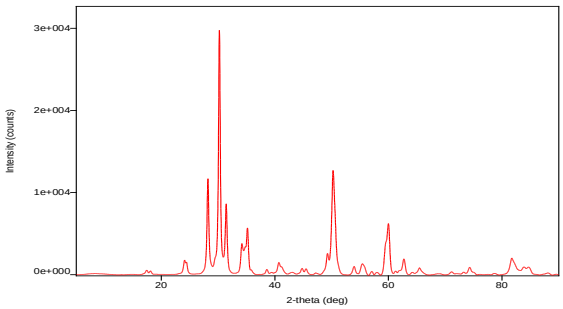


Figure 2.1:XRD of CSZ sample

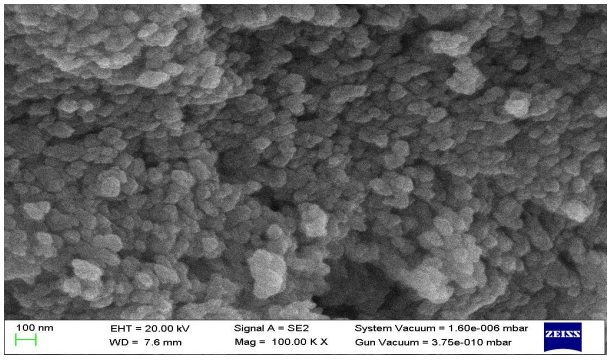


Figure 2.2: SEM of CSZ Sample

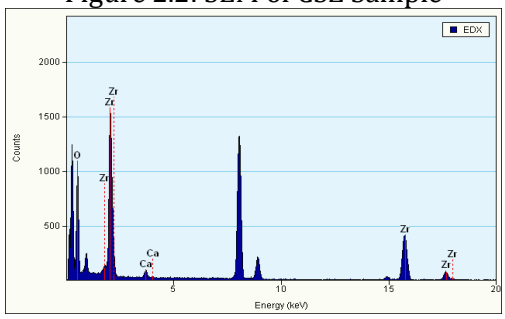


Figure 2.3:EDX of CSZ sample

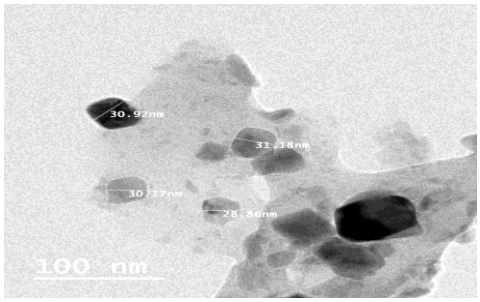
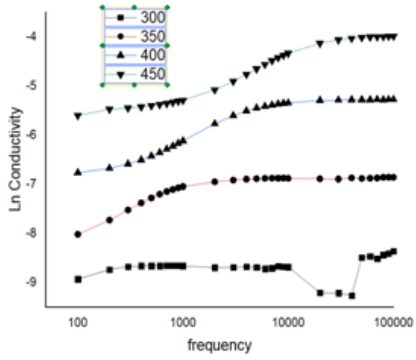


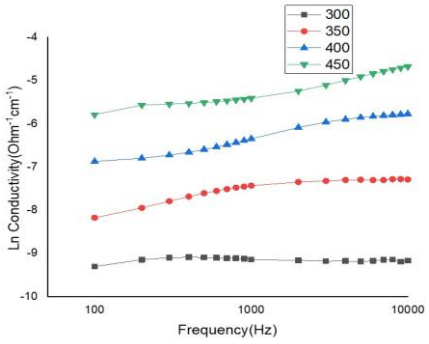
Figure 2.4: TEM of the CSZ sample

Two probe measurement method is used to determine the temperature dependency of AC electrical conductivity. The AC conductivity (σ) of the CSZ nanoparticles was calculated using the relation, $\sigma = 2\pi f \varepsilon_0 \varepsilon_r \tan\delta$

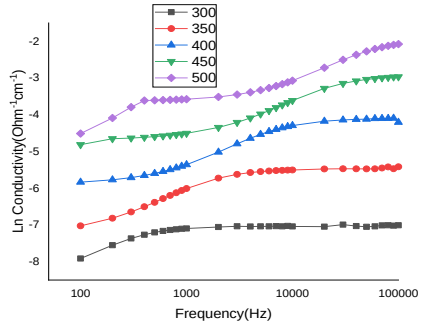
Because of ionic movement and electronic jumping to higher valence states, electrical conduction in Nano-CSZ takes place. Effect on the ac conductivity in the temperature interval from 300°C to 450°C w.r.t frequency is shown in Figure 2.5(a,b,c) of CSZ samples with 9%,12% and 15% mol wt of Calcia . With the increase in frequency from low to high, the ac conductivity increases in all temperatures gradually. When frequency is increased, frequency of hopping of electrons also gets improved which results in gradual increase in ac conductivity. Space charge polarization reduces at higher frequencies and hence the rate of increase of conductivity slows down at all temperature ranges in all compositions.



(a)



(b)



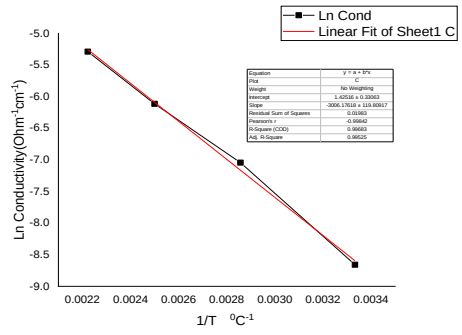
(c)

Figure 2.5 Frequency(Hz) dependence of conductivity of CSZ with a) 15% b) CaO, 12 % CaO, c) 9 % CaO

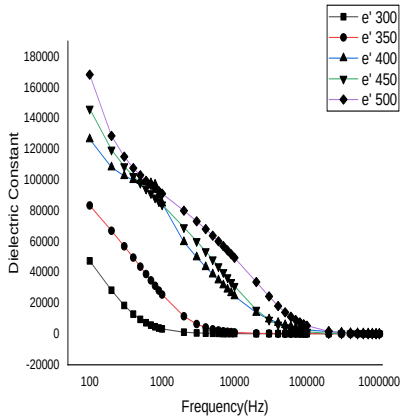
Activation energy required for electron hopping and movement of ions are found by fitting σ values into Arrhenius equation, $\sigma = \sigma_0 \exp[-E/kT]$

In the Arrhenius equation designations k, T and σ_0 refer to Boltzmann constant, absolute temperature and material constant respectively. From the figure 2.6, it is seen that with rise in temperature, conductivity (σ) increases. With the temperatures as seen in figure 2.6(a).After plotting, a linear fit is drawn to get the slope of the line and activation energy values are calculated. The activation energy of the CSZ nanoparticles is found to be 0.25 eV of 15% CaO, 0.21eV of 9% CaO and 0.27eV of 12% CaO CSZ samples. For SOFC (solid oxide fuel cell)

applications, activation energy should be lower and for the samples prepared activation energy is found in acceptable ranges[20]



(a)



(b)

Figure 2.6: a) Arrhenius plot depicting linear fit for CSZ sample with 15% CaO b) Variation of Dielectric constant with frequency of CSZ with 9% CaO

Effect of variation in frequency on the dielectric constant was measured for different temperatures 300°C to 500°C and plotted in figure 2.6 (b). The dielectric constant is calculated using the relation, $\varepsilon r = Cd/\varepsilon_0 A$, where d and A are the thickness of the sample and the area of the sample respectively [17]. The dielectric constant declines exponentially with increasing frequency for all temperatures, and eventually approaches a constant value in the high frequency area, as seen in the graph. Additionally, it is implied that as temperatures rise at low frequencies, the value of the dielectric constant rises as well. The combined impact of ionic, electronic, dipolar, and space charge polarisation causes polarisation in a material. At low frequencies, higher dielectric constant confirms presence of all types of polarization and with increase in frequency and temperature, dielectric constant exponentially gets reduced initially and then a gradual loss occurs. Electronic polarisation contributes very little to the decrease in dielectric constant. Since dipolar polarisation is inversely proportional to temperature, it is also anticipated that it will decrease with increasing temperature. [18,19]. The purity of the nanoparticles determines how much they assist to the polarizability of the space charge. [21-25]The presence of all four types of polarizations—space charge, orientation, electronic, and ionic polarizations—could illustrate the high dielectric constant at low frequencies, while the gradual loss of significance of these polarizations could clarify the low dielectric constant at higher frequencies.

3. CONCLUSION

Calcia stabilised zirconia nanoparticles were created under cryogenic surroundings by mechanical milling and decreasing their size. The structure, grain sizes purity of the powder samples was confirmed and ascertained from the XRD pattern, SEM, EDX and TEM. The calculated sizes were given in nanometers. Analysis was done on the relationship between the produced Nano-CSZ nanoparticles' dielectric constant and AC conductivity and variations in frequency and temperature. Studies reveals that dielectric constant decreased with the increase in frequency exponentially at all temperature for all prepared compositions. Investigators examined the impact of temperature and frequency on AC electrical conductivity and discovered that the conductivity rose as the temperature and frequency rose. Activation energy is found for 9,12,15 Mol% CSZ samples in range of 0.21-0.28eV which is in acceptable limits for SOFC applications[22].

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6. REFERENCES

[1] K.P. Jagannathan, S.K. Tiku, H.S. Ray, A. Ghosh, E.C. Subbarao, in: E.C. Subbarao Ed. , Solid Electrolytes and Ž . Their Applications, Plenum Press, New York, pp. 201–259,1980.

[2] D.G. Lamas, G.E. Lascalea, N.E.Walsöe de Reca,Synthesis and characterization of nanocrystalline powders for partially stabilized zirconia ceramics,Journal of the European Ceramic Society,Volume 18, Issue 9,Pages 1217-1221,1998.

[3] Ramamurthi SD, Xu Z, Payne DA. Nanometer-sized ZrO2 particles prepared by a sol–emulsion–gel method. Journal of the American Ceramic Society,Sep;73(9):2760-3,1990.

[4] A.K. Shukla, Vandana Sharma, N. Arul Dhas, K.C. Patil,Oxide-ion conductivity of calcia- and yttria-stabilized zirconias prepared by a rapid-combustion route,Materials Science and Engineering: B,Volume 40, Issues 2–3,Pages 153-157,1996.

[5] Mirosław M. Bućko,Ionic conductivity of CaO–Y2O3–ZrO2 materials with constant oxygen vacancy concentration,Journal of the European Ceramic Society,Volume 24, Issue 6,Pages 1305-1308,2004

[6] M. Zhou, A. Ahmad. Synthesis, processing and characterization of calcia-stabilized zirconia solid electrolytes for oxygen sensing applications. Materials Research Bulletin 41:690-696,2006

[7] Jianghong Gong, Ying Li, Zilong Tang, Zhongtai Zhang, "Enhancement of the ionic conductivity of mixed calcia-yttria stabilized zirconia", Materials Letters 46, Page. No. 115–119,2000.

[8] A comparison of microstructure and electrical Properties of 8 mol% yttria stabilized zirconia Processed under conventional, microwave, and fastfire Sintering techniques- Michael Ugorek, Thesis, Alfred University.2004

[9] R. Muccillo, R.C. Buissa Netto, E.N.S. Muccillo, "Synthesis and characterization of calcia fully stabilized zirconia solid electrolytes", Materials Letters 49 ,197–201,2001.

[10] Kannan M., Singh S., Prasad R.R. Synthetic Methods to Obtain Calcia-Stabilized Zirconia Powders—A Review. In: Manik G., Kalia S., Sahoo S.K., Sharma T.K., Verma O.P. (eds) Advances in Mechanical Engineering. Lecture Notes in Mechanical Engineering. Springer, Singapore. (2021), https://doi.org/10.1007/978-981-16-0942-8_39

[11] M. Asadikiya and Y. Zhong, "Oxygen ion mobility and conductivity prediction in cubic yttria stabilized zirconia single crystals," J. Mater. Sci., vol. 53, no. 3, pp. 1699–1709,2018.

[12] B. C. H. Steele, "Oxygen ion conductors and their technological applications," Mater. Sci. Eng. B, vol. 13, no. 2, pp. 79–87,1992.

[13] O.Y.Kurapova, O. V Glumov, M. M. Pivovarov, S. N. Golubev, and V. G. Konakov,"Structure and conductivity of calcia stabilized zirconia ceramics, manufactured from freezedried nanopowder," Rev. Adv. Mater. Sci., vol. 52, no. 1–2, pp. 134–141,2017.

[14] Thirupathy Maridurai, Dhanapal Balaji, Suresh Sagadevan, Synthesis and Characterization of Yttrium Stabilized Zirconia Nanoparticles,, Materials Research. 19(4): 812-816,2016.

[15] Raja Ram Prasad, K.L. Yadav, D. Puri, and B. S. S Daniel, , "Conductivity Measurement of Calcia Stabilized Zirconia prepared by Mechanical Route", Advanced Materials Research, 585, pp. 245-249,2012

[16] Kurapova O.Y., Glukharev A.G., Glumov O.V., Kurapov M.Y., Boltynjuk E.V., Konakov V.G. Structure and electrical properties of YSZ-rGO composites and YSZ ceramics, obtained from composite powder. *Electrochim. Acta*. 320:134573,2019.

[17] S.Suresh,Studies on the dielectric properties of CdS nanoparticles, Appl Nanosci 4:325–329,2014.

[18] Smyth CP, Dielectric Behavior and Structure. McGraw-Hill, New York,p 132,1965.

[19] Julia Ramírez-González, Anthony R. West, Electrical properties of calcia-stabilised zirconia ceramics, Journal of the European Ceramic Society, (2020), 10.1016/j.jeurceramsoc.2020.06.023.

[20] Jun Zhang, Christian Lenser, Norbert H. Menzler, Olivier Guillon, Comparison of solid oxide fuel cell (SOFC) electrolyte materials for operation at 500 °C,Solid State Ionics,Volume 344,115138, 2020.ISSN 0167-2738,https://doi.org/10.1016/j.ssi.2019.115138.

[21] Panwar, K, Murthy, D, S, "Analysis of thermal characteristics of the ball packed thermal regenerator", Procedia Engineering, 127, 1118-1125.

[22] Panwar, K, Murthy, D, S, "Design and evaluation of pebble bed regenerator with small particles" Materials Today, Proceeding, 3(10), 3784-3791.

[23] Bisht, N, Gope, P, C, Panwar, K, " Influence of crack offset distance on the interaction of multiple cracks on the same side in a rectangular plate", Frattura ed Integrità Strutturale" 9 (32), 1-12.

[24] Panwar, K, Kesarwani, A, "Unsteady CFD Analysis of Regenerator", International Journal of Scientific & Engineering Research, 7(12), 277-280.

[25] Singh, I., Bajpai, P. K., & Panwar, K. "Advances in Materials Engineering and Manufacturing Processes".