Synthesis of Ceria-Yttria, co-stabilized Zirconia (CYSZ) by Combustion Process for the application of thermal barrier coatings

Kavitha Rani N[1], Dr. M C. Jagath[2], Dr. K. N. Anuradha[3],Dr. Rajeshwari P[4], Dr Mahesh G. Emmi[5,*]

[1] Dept. of Industrial Engg. & Management, B.M.S. College of Engineering, Bengaluru, India.
[2]Dept. of Industrial Engg. & Management, Bangalore Institute of Technology Bengaluru, India.
[3]Dept. of Physics, Dr. Ambedkar Institute of Technology, Bengaluru, India.
[4]Dept of Industrial Engg and Management, Dr. Ambedkar Institute of Technology, Bengaluru, India
[4]Dept. of Chemistry, B.M.S. College for Women, Bengaluru, India
[5]Faculty of Management Studies and Advanced Technologies, Air Force Technical College, Bengaluru, India.

*Corresponding author
E-mail : maheshemmi@gmail.com

Abstract: In this paper, preparation of Ceria–Yttria co-stabilized Zirconia (CYSZ) Nanoparticles by solution combustion process was carried out. The crystallinity, stabilization of cubic crystalline phases was studied at different calcination temperature in the range of 500 to 1200° C by X-ray diffraction method (XRD). Surface morphology and compositional analysis were studied by Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray analysis (EDAX). EDAX showed dopants Cerium and Yttrium are present in the Zirconium lattice, FTIR resulted in concentration of dopants present in vicinity, with the Transition Electron Microscope (HRTEM) the particle size, crystallographic information and morphology were confirmed. The result show that nanoparticles prepared by solution combustion method can be possibly used for better Thermal Barrier Coatings due to the effects of the crystallite size on the reduction of thermal conductivity.

.

1. Introduction

Zirconium dioxide (ZrO_2) is a natural mineral called as baddelylite and ZrO_2 is also known as Zirconia. Baddelylite contains levels of Zirconia ranging from 96.5% to 98.5%. Zirconia has intrinsic physical and chemical properties, including chemical inertness, low thermal conductivity and high coefficient of thermal expansion (CTE) which closely matches that of the substrate and high melting temperature that make it attractive as a thermal barrier material. Zirconia has an elastic modulus close to steel (~ 200 GPa) and the mechanical property toughness and hence has greater range of properties [1]. In recent years, nanostructured zirconia based TBCs have received considerable attention because of some enhanced properties which is not found in conventional methods.

a) Thermal barrier Coatings(TBCs) TBC is the coating systems that protect the metallic components in gas turbine engines from the hot combustion gases. Their application allows an increase of combustion temperatures far beyond the melting point of the super alloys used for structural parts, such as blades and vanes. Although TBCs were introduced several decades ago, they are still a subject of intense research, both in acedemia and in industry. Considerable progress has been made through the years with respect to reliability, lifetime, and temperature capability, but still there is a need for further improvement of the properties to fully integrate the TBC system into the design of a gas turbine engine, and by this , to increse the efficiency of the engine. TBC using Ceria stabilized Zirconia applied to the combustion chamber of the internal combustion engine showed some improvement in fuel economy with a maximum of up to 4% at low engine power. The thermal Barriers coating found application as protective layers for steel surfaces of pistons and cylinders in Diesel engines and in case of elements of compressors housing for aircraft engines, made of titanium alloys, working surfaces of exhaust nozzles, made of niobium alloys,gas turbines and chemical plants made up of Nickel based alloys[2]. Aim of the paper is for the synthesis and preparation of CYSZ by solution combustion method for the application of Thermal barrier coatings in gas turbine engines.

b) Materials

1. **Zirconium Dioxide(ZrO_2)** Zirconia has the Molar Mass of 123.218 g/Mol undergoes disruptive phase changes into three phases and therefore it is called an allotropic form. The three phases are monoclinic at temperature less than 1167 C is tetragonal from 1167–2367 C, and cubic from 2367 C up to its melting point of 2677°C. The synthesized mixed metal oxide nanoparticles vary in physical, chemical, and morphological properties and are being used in various fields as they have various applications [3]. The resulting material with these changes in phases has superior thermal, mechanical, and electrical properties[4]. Different synthetic method have been used to synthesize zirconia nanoparticles which include- hydrothermal process [5] , biological synthesis [6] , co-precipitation [7] , solid state reaction [8] , microwave synthesis [9] and sol-gel method [10]. However, most of these synthesized nanoparticles are poorly crystalline or exhibit broad particle size distribution due to agglomeration [11, 12]
2. **Yttrium Dioxide(Y_2O_3)** Yttria which has the Molar Mass of 225.81 g/Mol is a vital starting point in inorganic synthesis of compounds. Yttrium oxide can also be used as additive in the coatings used in high-temperature applications, paints and plastics for guarding against UV degradation and in making permanent magnets.
3. **Cerium Dioxide (CeO_2)** Ceria which has the Molar Mass of 172.115 g/Mol occurs naturally as a mixture with other rare earth elements in its principal ores bastnaesite and monazite and adopts the fluorite structure. Cerium oxide due to potential uses result in many applications, such as high-storage capacitor devices, buffer layers for conductors, fuel cells, polishing materials, UV blocks and optical devices. CeO_2 is doped with ZrO_2 has shown significantly greater toughness and shown a good property in thermal barrier coating.

2. Experimental

a) Solution combustion synthesis Solution combustion synthesis (SCS) is a versatile, simple and rapid process, which allows effective synthesis of a variety of nanosized materials. This process involves a self-sustained reaction in homogeneous solution of different oxidizers (e.g., metal nitrates) and fuels (e.g., urea, glycine, hydrazides) [13]. The latest developments in SCS technique are discussed based on the materials applications. Many researches have carried out Sol-gel method for the preparation of CYSZ. Crystal structure investigated by XRD and Raman spectroscopy showed the tetragonal crystal structure of Zirconia, which was desirable for TBCs applications [14].

b) Combustion process Zirconylnitrate ($ZrO(NO_3)_2 6H_2O$), Ammonium ceric nitrate($(NH_4)_2Ce(NO_3)_2$) and Yttrium nitrate hexahydrate($Y(NO_3)_3$ $6H_2O$) were synthesized by using Glycine(NH2CH2COOH) as fuel dissolved in minimum quantity of de-ionized water in a 250ml borosil glass beaker. The F/O ratio was maintained to be unity to ensure complete combustion. The excess water was evaporated to get a highly viscous transparent gel resulted yellow in color. This viscous transparent gel was transferred into a domestic microwave oven. Initially the solution was vigorously boiled and underwent dehydration followed by catching of the fire leading to the liberation of the enormous amount of the gases like CO_2, N_2 and water vapours and finally led to the formation of the highly swelling, porous and voluminous puffy white and yellow powder for different composition of CYSZ[15][16]. The schematic process is depicted in Figure 1.

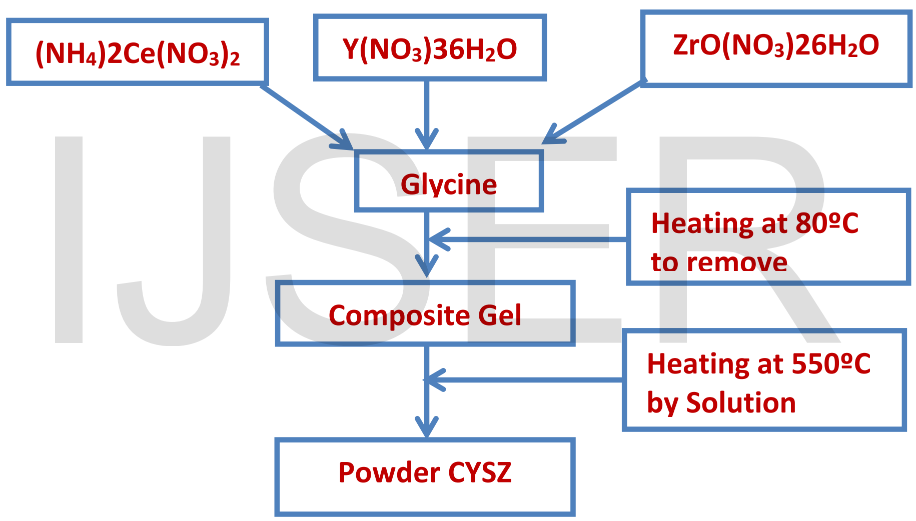


Figure 1 Methodology adopted for preparation of CYSZ powder

c) Synthesis of ZrO_2, CeO_2 and Y_2O_3 nanoparticles Pure Zirconia has no significance on any application particularly as TBCs, this is due to transformation of tetragonal phase of Zirconia to monoclinic at 950°C and this results in catastrophic failure. Addition of variety of oxides like CeO_2 and Y_2O_3, suppresses the high temperature transition which is essential for coating materials. CSZ ceramics can attain significantly greater toughness resistance than YSZ and also it is thermal shock resistance. YSZ ceramics resulted in indication of erosion resistance which is not possible with CSZ. To solve this, one possibility is addition of all the three constituents mixtures of Ceria, Yttria and co stabilized Zirconia(CYSZ) can be synthesized for the application of TBC. Many researchers have found the application of CYSZ and have prepared the by different techniques. In this paper nanoparticles Ceria, Yttria, and Zirconia were synthesized by the combustion process.For the different proportion of Stoichiometric preparation, nitrates Zirconyl nitrate ($ZrO(NO_3)_2$ $6H_2O$), Ammonium ceric nitrate($(NH_4)_2Ce(NO_3)_2$) and Yttrium nitrate hexahydrate($Y(NO_3)_3$ $6H_2O$)

ISSN 2229-5518

were used for synthesis.All the three nitrates were dissolved in minimum quantity of de-ionizedwaterina250ml borosil glass beaker. To these precursors varied amount of glycine (NH_2CH_2COOH) was added and mixed thoroughly. Samples with varying percentage of glycine were synthesized by combustion process. Samples were labeled as CYSZ-11,CYSZ-12,CYSZ-13 and CYSZ-14. The structure and the texture of the nanoparticles depend on the synthetic method and the precursor used [17].

Table 1: Calculated Air fuel ratio

Zirconyl nitrate ($ZrO(NO_3)_2 6H_2O$	**Ammonium ceric nitrate ($(NH_4)_2Ce(NO_3)_6$**	**Yttrium nitrate hexahydrate $Y(NO_3)_3 6H_2O$**	**Glycine (NH_2CH_2COOH)**
10	**24**	**15**	**9**

Table 2: Samples with varying percentage of glycine synthesized by microwave combustion

Synthesised Samples With different compositions for analysis	**Fuel Air Ratio calculation for synthesizing CYSZ**			
	Zirconyl nitrate (grams)	Ammonium ceric nitrate (grams)	Yttrium nitrate hexahydrate (grams)	Glycine (grams)
CYSZ-11	2.288187	0.56034	0.35022	3.198747
CYSZ-12	2.26484	0.840446	0.52535	3.630636
CYSZ-13	2.241493	1.120746	0.700466	4.062705
CYSZ-14	2.218144	1.400928	0.87558	4.494652

d) Charactrization of Synthesized CYSZ The CYSZ nanoparticles synthesized from microwave combustion method are characterized by various analytical techniques as follows:

1.Peak analysis using XRD, the X-ray diffraction (XRD) of powder samples was measured using X-raypowder diffractometer (Panalytical's X'pert3powder diffractometer, source Cu-Kα, λ¼1.5418Å) operated in reflection mode.

2.Bonding strength using FTIR, Fourier Transform Infrared(FTIR) spectra was recorded Perkin-Elmer spectrometer)with KBr pellet technique.

3.Morphology of the nanoparticles using SEM, the morphology of the CYSZ nanoparticles were studied by Field emission Scanning Electron Microscope(FESEM) with EDX (GEMINI,Ultra 55).SEM shows CYSZ at different composition of Cerium Oxide from 0.3 to 0.5 grams, Yttrium oxide 0.1 to 0.3 grams and Zirconium dioxide 0.94 to 0.98 grams molar ratio.

4.Particle size and shape analysis,the particle size and shape of CYSZ nanoparticles were recorded using High Resolution Transmission electron Microscope (HRTEM). The phase formed was reconfirmed by using SAED pattern from TEM(JOEL/TEM2100)

3. Results and Discussions

a) Scanning Electron Microscope In order to examine the morphology and the elemental composition, the samples are subjected to SEM with EDX analysis. The SEM images of the nanoparticles synthesized by Solution Combustion and calcined at different temperature as shown in the Figure 2 (a,b,c,and d). The SEM structures of CYSZ obtained also shows that a porous network in all the samples as a consequence of gases escaping during the combustion process. It shows that the samples are uniform with well-defined morphology of each particle. It is obvious that with increasing the calcination temperature the particles become bigger.

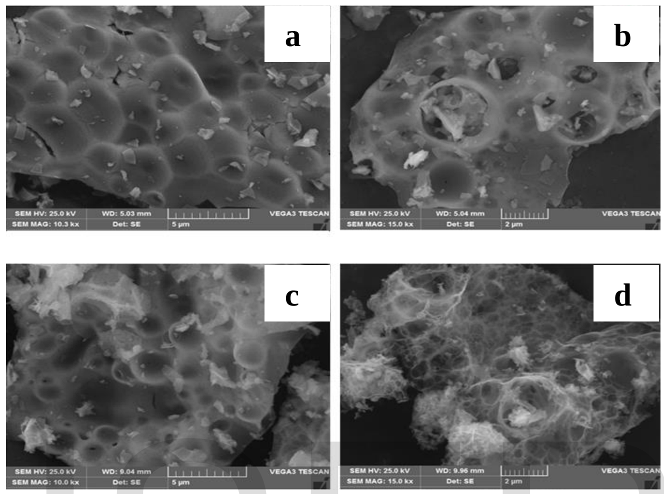
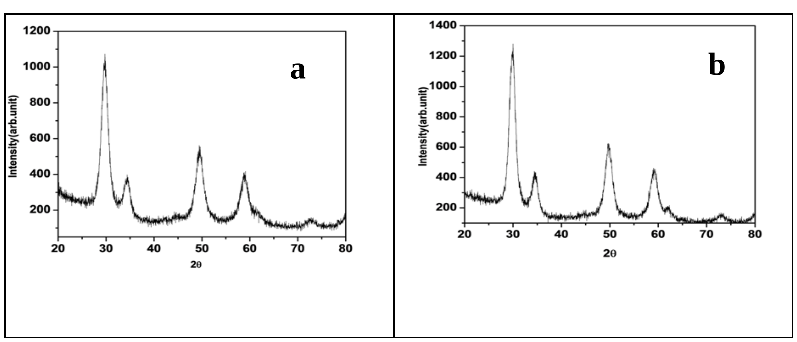


Figure 2 (a, b, c and d): Showing the Scanning Electron Microscope (SEM) structures of CYSZ-11, 12, 13 and 14 nanoparticles respectively.

b) X-Ray Diffraction The XRD results in Figure 3(a, b, c and d) shows that the reflection obtained are matching with JCPDS Card No. -01-079-1771, shows that the porosity increases with various concentrations of Cerium and Yttrium and hence due to this the particle size decreases. The XRD patterns reveal the fact that the synthetic methods play an important role in the phase formation as well as the crystalline size of the ZrO_2 nanoparticle. The diffraction peaks in Figure 4, confirms the formation of tetragonal ZrO_2 structure for all samples without any impurity or secondary phase and this shows that the synthesis is good. The peak in all samples indicates the presence of tetragonal phase of ZrO_2.



ISSN 2229-5518

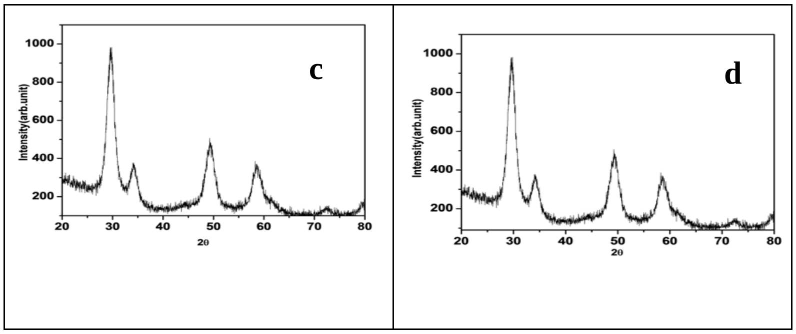


Figure 3 (a, b, c and d) X-ray diffraction (XRD) of powder samples was measured using X-raypowder diffractometer for CYSZ-11, 12, 13 and 14 nanoparticles respectively

c) Energy Dispersed X ray Analysis The chemical composition of the ZrO_2 nanoparticles obtained through microwave method was analyzed by means of energy dispersed X-ray analysis(EDX) shown in the Figure 4. This depicts, the dopants Cerium and Yttrium are present in the Zirconium lattice in the sample CYSZ-11.

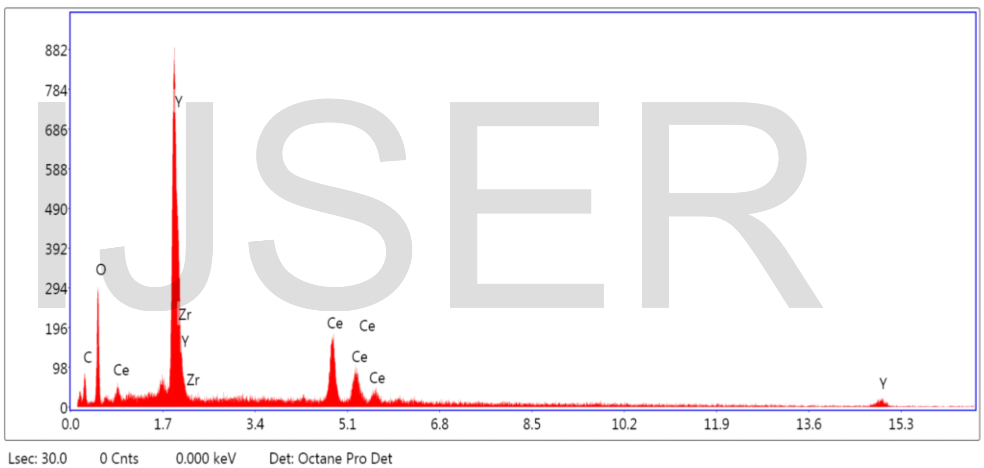


Figure 4 EDX analysis of CYSZ-11 sample

d) Transmission Electron Microscope TEM micrographs shows CYSZ calcined with various magnification. The Figure 5 shows that the ZrO_2 nanostructures are hexahedron shaped particles. The dark spot inside the grey matrix indicates the **tetragonal Zirconia in Ceria and Yttria matrix.**

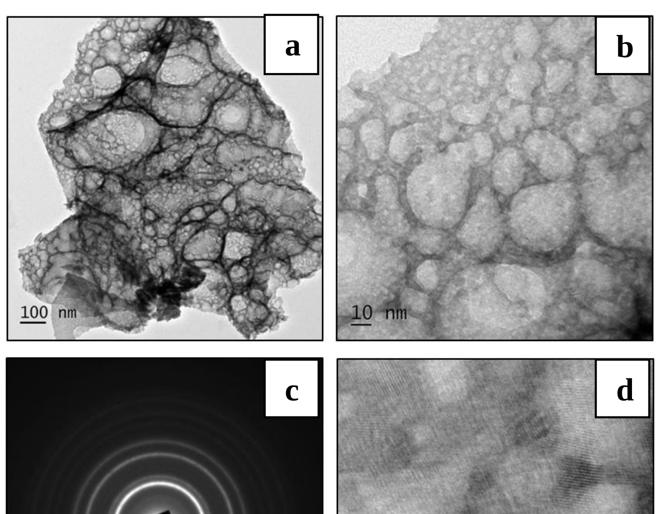


Figure 5 Showing the Transmission electron micrograph of CYSZ calcined with various magnification

e) Fourier Transform Infrared (FTIR) From the Figure 6, it is found that the stretching frequency at the vicinity of 597Cm^{-1} shifts to the lower wave number region as the concentration of dopant ions increases. A stretching frequency at 1368 due to OH bending and a broad peak at 3400 are due to bending frequency of adsorbed moisture.

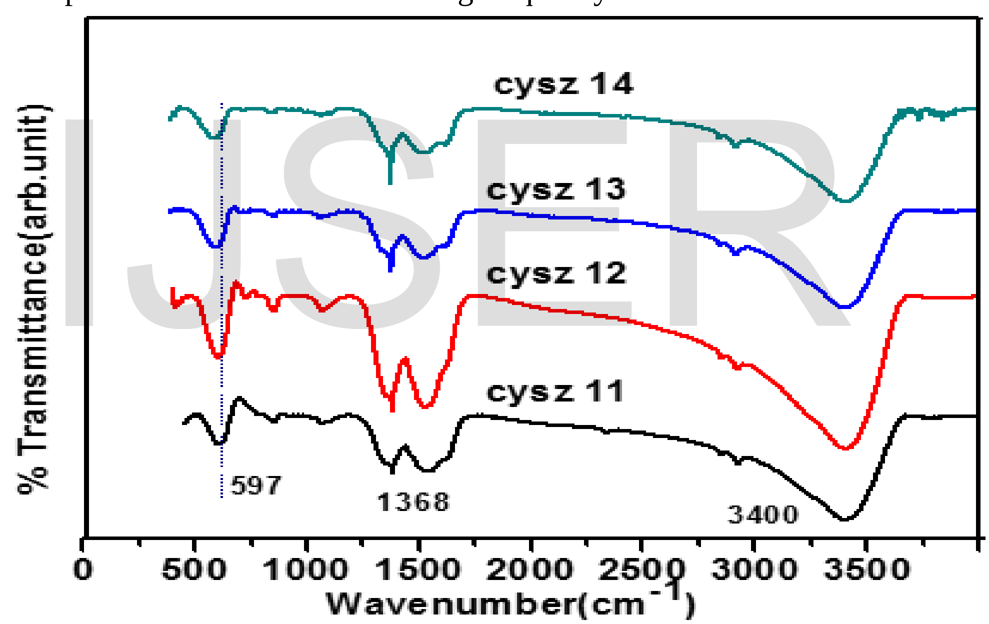


Figure 6 Fourier Transform Infrared micrograph of different samples

4.Conclusions

The synthesis of Zirconia with dopant Ceria and Yttria was prepared by combustion process using Glycine as the fuel, with various composition of glycine many samples of CYSZ were prepared, characterization was done with various techniques like XRD, SEM, FTIR and TEM. XRD revealed the tetragonal structure of Zirconia which very well suits for thermal barrier coatings for applications at more than 1000^0 C. Further the samples have to be tested for sintering behaviour which has to be worked at elevated temperature at 1200^{0}C or more and processed for TBC. In this paper Ceria and Yttria are co-stabilized with Zirconia, but on prolonged exposure to temperatures in excess of 1200^{0}C Yttria segregates into high and low concentration tetragonal phases, on slow cooling the low Yttria phase transforms into monoclinic phase with resultant volume expansion and this induces cracking within coating and results in failure[18,19]. Ceria and Yttria co-stabilized with Zirconia will establish good result for thermal barrier coating, this aspect has scope for further investigations. Combustion fuel used in this work is Glycine, research can be done by using Citric Acid and Urea for the synthesis of CYSZ and can be tested for thermal barrier coating.

Acknowledgements

The present work was supported by department of Industrial Engineering and Management, Chemistry Department and Mechanical Engineering Department, B.M.S. College of Engineering, Bengaluru, India.

References

[1] S T. Aruna, Alexander S. Mukasyan, Combustion synthesis and nanomaterials, current Opinion in solid State and Materials Science12(2008)44-50.

[2] Mridula Biswas, Prasant Kumar Ojha, E. Moses Jayasingh and C. Durga Prasad, Synthesis of nanocrystallineYttria stabilized Zirconia for SOFC, INTECH open access publisher.

[3] Pramesh N. Kapoor, Ajay Kumar Bhagi, Ravichandra S. Mulukutla, Kenneth J. Klabunde. "Mixed Metal Oxide Nanoparticles". Dekker Encyclopedia of nanosciences and nano technology. 2004 DOI: 10.1201/NOE0849396397.ch197

[4]L. Li, O. Van Der Biest , P. L. Wang, J Vleugels, W W Chen, S G Huang, Estimation of the phase diagram for the ZrO2-Y2O3-CeO2 system, Journal of the European Ceramic Society 21(2001) 2903-2910

[5] E H Kisi and C J Howard, Crystal Strcutures of Zirconia Phases and their Inter-Relation, Key Engineering Materials, Trans Tech Publication , Vol 153-154, pp 1-36

[6] Morteza Hajizadeh- oghaz, reza Shojarazavi, Ali Ghasemi, Synthesis and characterization of ceria-yttria co stabilized zirconia (CYSZ) nanoparticles by Sol-gel process for thermal barrier coatings(TBCs) applications, (2015)74:603-612

[7] Tatiana. M. Arantes., Giovanni. P. Mambrini., Daniel. G. Stroppa., Edson. R. Leite., Elson. Longo., Antonio. J. Ramirez., Emerson. R. Camargo. "Stable Colloidal Suspensions of Nanostructured [Ayanwale et. al., Vol.6 (Iss.8): August 2018 ISSN- 2350-0530(O), ISSN- 2394-3629(P)

[8] Padma. Nimare., A. A. Koser. "Biological Synthesis of ZrO2 Nanoparticle using Azadirachta Indica Leaf Extract. IRJET Vol.3 Issue: 07 July 2016. P-ISSN: 2395-0072, e-ISSN: 2395-0056.

[9] K. Geethalakshmi., T. Prabhakaran., J. Hemalatha. "Dielectric Studies on Nano Zirconium Dioxide Synthesized through Co-precipitation Process." Intl. J. of Mater. & Metallurgical Engineering. Vol. 6, No. 4, 2012.

[10] Xinmei. Liu., Gaoqing. Lu., Zifeng. Yan. "Preliminary synthesis and characterization of mesoporous nanocrystalline zirconia." Journal of Natural Gas Chemistry, Vol. 12, No. 3, 2003.

[11] A.K. Singh., Umesh. T. Nakate. "Microwave Synthesis, Characterization and Photoluminescence Properties of Nanocrystalline Zirconia". The Scientific World Journal Volume 2014, Article ID 349457, 7 pp http://dx.doi.org/10.1155/2014/349457

[12] R. Madhusudhana., M.A. Sangamesha., R. Gopal. Krishne. Urs., L. Krishnamurthy., G.L. Shekar. "Synthesis and Characterization of Zirconia by Simple Sol-Gel Route." International Journal of Advanced Research (2014), Volume 2, Issue 4, 433-436. ISSN: 2320-5407

[13] Chenguo. Hu., Zuwei. Zhang., Hong. Liu., Puxian. Gao., Zhong. Lin. Wang. "Direct Synthesis and Structure Characterization of Ultrafine CeO2 Nanoparticles." Nanotechnol. 17(2006) 5983-5987. DOI: 10.1088/0957-4484/17/24/013

[14] Haritha. Meruvu., Meena. Vangalapati., Seema. Chaitanya. Chippada., Srinivasa. Rao. Bammidi."Synthesis and Characterization of Zinc Oxide Nanoparticles." Rasayan J. Chem. Vol.4, No.1 (2011), 217- 222. ISSN: 0974-1496. CODEN: RJCABP

[15] Thakare, Progress in Synthesis and Applications of ZirconiaInternational Journal of Engineering Research and Development e-ISSN: 2278-067X, Volume 5, Issue 1 (November 2012), pp 25-28

[16] IngeborgKaus, Paul Inge Dahl, Johann Mastin, Tor Grande, and Mari-Ann Einarsrud Synthesis and Characterization of Nanocrystalline YSZ Powder by Smoldering Combustion Synthesis Volume 2006, Article ID 49283, pp 1–7

[17] S. Rossignol., Y. Madier., D. Duprez. "Preparation of zirconia-ceria materials by soft chemistry." Catalysis Today, vol. 50, no. 2, pp 261–270, 1999.

[18] S. Manjunatha, S.Dharmaprakash Microwave assisted synthesis of cubic Zirconia nanoparticles and study of optical and photoluminescence properties.

[19] Nicholas Curry, Wyszomir Janikowski, Zdenek Pala, MonilaVilemova and Nicolaie Markocsan Impact of Impurity Content on the Sintering Resistance and Phase Stability of Dysprosia and Yttria Stabilized Zirconia Thermal Barrier Coatings, Volume23, 2014