

Processing & Characterization of Stabilized Zirconia using dolomite

A Thesis Submitted in
Partial Fulfillment of the Requirement
for the degree of
BACHELOR OF TECHNOLOGY

By
BIPIN KUMAR SINGH



DEPARTMENT OF CERAMIC ENGINEERING
NATIONAL INSTITUTE OF TECHNOLOGY ROURKELA
MAY 2007

Processing & Characterization of Stabilized Zirconia using dolomite

A Thesis Submitted in
Partial Fulfillment of the Requirement
for the degree of
BACHELOR OF TECHNOLOGY

By
BIPIN KUMAR SINGH

Under the Guidance of
S. Bhattacharyya
Prof & HOD



DEPARTMENT OF CERAMIC ENGINEERING
NATIONAL INSTITUTE OF TECHNOLOGY ROURKELA
MAY 2007

Certificate

This is certified that the work contained in the project entitled “Preparation and Characteristics of tetragonal phase zirconia using dolomite” by Bipin Singh, have been carried out under my supervision and that this work has not been submitted elsewhere for a degree.

(S. Bhattacharyya)

HOD

Department of Ceramic Engineering

National Institute of Technology

Rourkela

Acknowledgement

I express our deep gratitude to our honored guide, Dr. S. Bhattacharyya, Professor of Department of Ceramic Engineering, NIT Rourkela, for the valuable advice and guidance in the completion of this project work. I greatly indebted to him for instilling in me the idea and structure of this project.

I record our sincere appreciation to Dr. S Pratihari professor of the Department of Ceramic Engineering for providing me the necessary facilities.

My heartfelt thanks to all the faculty members for their critical suggestions and encouragement during this project work. I sincerely acknowledgements to the non teaching staff and faculty for the help and cooperation extended to us during the completion of the project.

I specially thanks to Mr. R.P. Rana, Research Scholars of the Department of Ceramic Engineering, for helping me out with my project in certain characterization of the samples and allowing me the use of certain equipments.

And finally, my heartfelt thanks to all my friends who have constantly helped, encouraged, boosted my morale and have worked with me in completing this dissertation work.

BIPIN KUMAR SINGH
10308002

Contents

CHAPTER	PAGE
CERTIFICATE	I
ACKNOWLEDGEMENTS	II
ABSTRACT	III
LIST OF FIGURES	IV
SYNOPSIS	V
1. INTRODUCTION	
2. LITERATURE REVIEW	
2.1 Synthesis of CSZ by solid state route.	12
2.2 Synthesis of YSZ by chemical route.	12
2.3 Synthesis of PSZ by chemical route.	13
2.4 Injection molding route.	13
2.5 Synthesis of Y-TZP by solid state route.	13
2.6 Plasma spraying (APS) or electron-beam physical-vapor-deposition.	14
2.7 Molecular decomposition method.	14
2.8 Synthesis of MgO-PSZ by solid state route	15
2.9 Sol-gel synthesis	15
2.10 Synthesis of Ca-PSZ/WC by solid state reaction.	15
2.11 By solid-solid diffusion process.	16

3.	EXPERIMENTAL	
	3.1. Raw Material	17
	3.2. Batch Composition	17
	3.3. Preparation	18
	3.4. Formation of 3% PVA	19
	3.5. Addition of PVA	19
	3.6 Flow Chart	20
	3.7 Characterization	20
4.	RESULTS AND DISCUSSION	21-28
5.	CONCLUSIONS	29
	REFERENCES	30-31

Abstract

Tetragonal zirconia polycrystal ceramics were stabilized by three different type of dolomite (white, black, cream).The TZP powders were synthesized by co-precipitation method using $ZrOCl_2$ and 3,4,5,6mol% dolomite solution with HCl .The precipitated gel were washed to give soft agglomerate with higher green density. The powder exhibited the tetragonal phase at 850°C temperature due to their small crystallite size. The phase evolution was the function of calcinations temperature. The densification behaviour shows a higher shrinkage rate for the compacts with white dolomite stabilized. These powders were compacted by uniaxial pressing and fired at 1400 to 1600°C for 4hrs.The relative density was higher for white dolomite stabilized TZP as compared to the other two for all sintering temperature and also it will increasing with temperature. This also retained the metastable tetragonal phase. The observed sintered compacts show an isotropic shrinkage which explains the better density and high hardness and compressive strength (in case of black dolomite) even at higher temperature.

List of figures

Figure No	Name of the Figure	Page No.
1	XRD of different calcine powder with varying dolomite mol% and temperature.	21-22
2	XRD of different sintered sample with varying dolomite mol% and temperature.	23-24
3	Apparent density with varying temperature and mol% of dolomite.	25-26
4	Relative density with varying temperature and different type of dolomite	27
5	Strength varying with temperature	27
6	Hardness with varying composition.	28

Synopsis

These days a lot of research is going on for the development better refractory bricks for high temperature industrial applications. At high temperature brick loss some properties like thermal stability, chemical stability. The stabilized zirconia using dolomite has good conductivity, high mechanical stability, thermal stability, chemical stability at high temperature. Therefore they have been used in steel industry and other high temperature application. In this project we prepare stabilized zirconia using different type of dolomite and different composition variation through chemical route. We mainly study the phase evolution and phase stability of the materials through the XRD analysis.

The XRD patterns of the dolomite synthesized TZP samples at different temperatures shows sharp well defined peaks which shows the high crystalline nature of the synthesized phase without any impure phase. All the peaks are matched well with the characteristics of the parent compounds.

Interest in zirconia-based ceramics is attributed to their unique set of properties. The very high melting temperature of zirconia makes it a prime candidate for refractory applications. Zirconia is a candidate material for components that are subjected to high thermal shock resistance, high temperature and corrosive environments. Zirconia has been utilized in seals, engines, cutting tools, sensors, and thermal barrier coatings [1]. Pure zirconia undergoes a number of reversible phase transitions during heat treatment. The most destructive is the transformation of tetragonal to monoclinic phase resulting in 4% volume change [2]. The best method to exploit the properties of zirconia is improvement of sinterability by stabilization of the high temperature phases to room temperature. Control over the stability is achieved by doping zirconia with one or more of the fluorite stabilizer oxides [3]. CaO [4], MgO [5], Y₂O₃ [6] and CeO₂ [7] are used to achieve either fully or partially stabilized zirconia. Calcia and magnesia are the most extensively used oxides to stabilize zirconia at their high temperature polymorphs because of their cheap precursors and refractory potential [8]. However, CaO and MgO stabilized zirconia show poor stability due to the extensive tetragonal to monoclinic phase transformation resulting in extensive cracking in certain applications [9]. Precipitation, eutectoid decomposition, and crystallization of zirconia proceed very slowly and equilibrium is difficult to achieve. Wu et al. [10] found that high density and small grain size can be achieved by the use of multiple additives i.e. CaO (or Y₂O₃) together with MgO. Calcia (12 mol%) stabilized zirconia (CSZ) powders showed the coexistence of monoclinic and cubic solid solutions between 1180 and 1325 °C. In sintered samples, the cubic solid solution decomposition reaction follows the metastable extension of the boundary line separating the two-phase regions from that of the cubic solid solution. On cooling, tetragonal solid solution precipitate forms within the cubic matrix and partially transforms into monoclinic on cooling [11]. Different routes have been utilized for processing of fine powders including co-precipitation [12], alkoxide [13], and citrate routes [14]. The main defect is the agglomeration of powders [15]. In the current work,

urea formaldehyde polymeric gels were used as a precursors for the synthesis of 12 mol% (Mg, Ca)-PSZ. Phase analysis and microstructure characteristics were assessed.

Stabilized zirconia is known to be due to the oxygen ion mobility caused by doping with lower valent metal ions or metal ions of different ionic sizes. It is either a cubic or tetragonal structure can be developed in zirconia by incorporation of dopants such as Y^{3+} , La^{3+} , Mg^{2+} , Ca^{2+} , etc. Ce-TZP and Y-TZP ceramics have high fracture toughness and high thermal stability. [16] However, yttria-doped TZP ceramics present low temperature degradation in moist environments due to the solubilization of Y_2O_3 to its hydroxide. It was also found that the serious decrease of fracture toughness should be predominantly caused by low transformability in the reduced Ce-TZP. [17] Calcia addition is preferred over other oxides due to stability of cubic phase at all temperatures [19]. Where as the magnesia or yttria-stabilization revert to the monoclinic structure at low temperatures. While using calcia and magnesia as stabilizer in zirconia, the toughening of the material increases, by the mechanism known as transformation toughening [20]. A significant limiting factor with these toughening properties increases with increasing temperature of the material serves to stabilize the tetragonal phase thus reducing the propensity for the precipitates to undergo a stress-induced transformation to the monoclinic phase [21]. In order to circumvent this problem, an attempt has been made to utilize other potential toughening mechanisms that are temperature insensitive to improve the high temperature toughness of TZP-type materials, while retaining the transformation mechanism at low temperatures. [22]. The aim of this present work is to select the best dolomite out of the three (back, white, cream) for achieving higher density, t-phase and better mechanical property at room temperature

Durrani et al [1] studied five weight percent calcia stabilized zirconia (CSZ). This material was synthesized from zirconia and calcia powder by solid state reaction. Powder specimens were sintered at various temperatures for different time durations in air and argon atmosphere. Physico-chemical properties such as thermal stability, purity, crystalline phases identification, particle size, particle size distribution, specific surface area and porosity of CSZ were measured by thermogravimetry and differential thermal analysis (TG/DTA), X-ray diffraction (XRD), scanning electron microscopy (SEM), Brunauer–Emmett–Taller (BET) and particle size analyzer (PSA). Total relative shrinkage and coefficient of thermal expansion were estimated by dilatometry. The density and Vicker's micro hardness were measured in order to evaluate the material performance. A combination of cubic zirconia and calcium zirconium oxide ($\text{Ca}_{0.15}\text{Zr}_{0.85}\text{O}_{1.85}$) phases were found when specimen sintered at 1500 °C in air while under argon atmosphere at 1750 °C and 1850 °C, the ZrO and $\text{Ca}_{0.15}\text{Zr}_{0.85}\text{O}_{1.85}$ phases were established. At higher sintering temperature (1950 °C) for 4 h in argon medium three phases ZrO, CaZrO_3 and $\text{Ca}_{0.15}\text{Zr}_{0.85}\text{O}_{1.85}$ were observed. It was found that with the increase of sintering time these phases convert into a single cubic phase $\text{Ca}_{0.15}\text{Zr}_{0.85}\text{O}_{1.85}$. Pellets sintered at different temperatures and duration was also studied by scanning electron microscopy showing that the grain structure becoming fine with increase of temperature and duration.

Patsias et al [2] synthesized yttria-stabilized zirconia by following chemical route technique and investigated the temperature and composition dependence on the mechanical properties and crystalline structure. Yttria-stabilized zirconia, deposited by air plasma spraying (APS) or electron-beam physical-vapor-deposition (EB-PVD) on Inconel beams. The loss factor and Young's modulus of the coating were estimated as a function of strain amplitude with the aid of a numerical analysis. It was found that the coating produced by APS has higher damping, lower elastic stiffness and stronger

amplitude dependence than that produced by EB-PVD. These features are correlated with the microstructure examined by scanning electron microscopy.

Jensen et al [3] synthesized partially stabilized zirconia alloy by chemical route and doping 10.8 mol% Mg-PSZ with 1.25 mol% CeO₂. This material had a microstructure that had oblate spheroidal precipitates having twice the diameter and aspect ratio of those in Mg-PSZ. These precipitates enhanced the toughness through toughening mechanisms other than the usual transformation toughening mechanism operating at elevated temperatures. There is a measurable toughening at high temperature that cannot be attributed to transformation toughening. However, more work is required in the processing to reduce the porosity of the material.

Wen-Cheng et al [4] studied the effect of the mixture of coarse fine ZrO₂ powder in various ratios the properties of injection molding feed stock ,the degree of debinding ,dimension reproducibility, sintering and phase formation of the Mg-partially stabilized zirconia (PSZ) were studied. The feedstock and injection molding pieces with 3.5wt% MgO were tested by capillary rheometry, thermal analysis (DSC), and the injectionmolded pieces were analyzed by SEM and quantitative XRD techniques. Experiment result show when the feedstock contained > 50 vol% of coarse powder ,the viscosity is lower and activation energies of feed stocks are in the same range as that of pure binder admixture. The flowing properties are controlled by fine to coarse as the concentration of fine powder as over 50vol% in addition, the formulation with higher content in fine powder would enhance the de-polymerization of PP, improve the dimensional reproducibility, homogeneity, degree of debinding .With the appropriate controls on the ratio of fine to coarse powder, Mg-PSZ with 60to 93 % theoretical density and uniform microstructure can we produced.

Yang et al .[5] studied the wear behaviors of yttria-doped tetragonal zirconia polycrystal (Y-TZP) ceramics with different microstructures worn against diamond wheel under various wearing conditions and compared to that of dense magnesia-doped partially stabilized zirconia Mg-PSZ.and fine-grain Al₂O₃. A block-on-wheel tribometer with unidirectional sliding was used to carry out the wear experiments. The friction coefficient

of dry sliding was recorded. The worn surfaces of these materials were also characterized by X-ray diffractometry_XRD, scanning electron microscopy_SEM.and surface profilometry. The wear resistance of worn pieces were analyzed and determined. The possible wear mechanisms and a master wear equation of the ceramics are proposed and discussed.

Patsias et al [6] studied the mechanical damping and elastic stiffness of ceramic coatings, of yttria-stabilized zirconia, deposited by air plasma spraying (APS) or electron-beam physical-vapor-deposition (EB-PVD) on Inconel beams. The loss factor and Young's modulus of the coating have been estimated as a function of strain amplitude with the aid of a numerical analysis. It has been found that the coating produced by APS has higher damping, lower elastic stiffness and stronger amplitude dependence than that produced by EB-PVD. These features are correlated with the microstructure examined by scanning electron microscopy.

Emad et al [7] studied urea-formaldehyde resin was used as a precursor for the processing of ultrafine 12 mol%(Mg ,Ca)-PSZ powder with uniform morphology .12 mol% CaO Stabilized zirconia was subjected to extensive cracking on reheating between 1400⁰C and 1500⁰C. The cracking phenomenon was found to be due to the tetragonal to monoclinic phase transformation. MgOequal to CaO was added at 3.6 and 9.mol% to improve the stability of tetragonal zirconia .The Crystallization of tetragonal zirconia from the amorphous powder occurs between 400and 500 .The stability of tetragonal phase zirconia was found to increase with addition of MgO.The addition of MgO ,combined with fast heating during hot pressing ,activates the densification process by acting as a sintering aid and reducing the relative degree of structural coarsening .Optimized stability of tetragonal zirconia and good microstructure were achieved at equal proportions of MgO and CaO.

Qingguo et al [8] studies the synthesis of MgO-PSZ by solid state route. The thermal expansion characteristics of MgO partially stabilized zirconia (MgO-PSZ) electrolytes were studied by dilatometric technique. It is found that the phase transformation of MgO-

PSZ from monoclinic to tetragonal takes place in two temperature ranges of 460–830°C and 1150–1180°C. The volume shrinkage associated with these phase transformations plays an important role for the thermal shock resistance. With heat-treatment at 1300°C for 2 h and at 1000°C for 6–8 h, the thermal shock resistance of the MgO-PSZ electrolyte tube can be greatly improved.

Norbert [9] studies the wear behaviors of yttria-doped tetragonal zirconia polycrystal_Y-TZP ceramics with different microstructures worn against diamond wheel under various wearing conditions were investigated and compared to that of dense magnesia-doped partially stabilized zirconia_Mg-PSZ and fine-grain Al₂O₃. A block-on-wheel tribometer with unidirectional sliding was used to carry out the wear experiments. The friction coefficient of dry sliding was recorded. The worn surfaces of these materials were also characterized by X-ray diffractometry_XRD, scanning electron microscopy_SEM and surface profilometry. The wear resistance of worn pieces were analyzed and determined. The possible wear mechanisms and a master wear equation of the ceramics are proposed and discussed.

Emilio Jimenez et al [10] studies the effect of zirconia polycrystals stabilized with 7 mol. %CaO containing 10 vol. %WC particles (Ca-PSZ/WC) were obtained by using zirconia nanopowder and WC micropowder. Cold isostatically pressed samples were pressure less sintered in argon at 1350–1950 °C. The influence of the sintering temperature and the incorporation of WC particles on the phase composition and mechanical properties of the composites were studied. Decomposition of WC due to the reaction with the zirconia matrix was found. W₂C and metallic tungsten were detected as decomposition products when heat treated below 1750 °C. At higher temperatures, ZrC is formed. The mechanism of WC decomposition was discussed. The zirconia polycrystals modified with in situ formed W and W₂C inclusions showed a bending strength of 417±67 MPa, a fracture toughness of 5.2±0.3 MPa·m^{0.5} and a hardness of 14.6±0.3 GPa.

[11] Studies the sintering of $ZrO_2.MgO.ZnO$ powder has been investigated by TMA(Thermal Mechanical Analyser) and its phases analysed by XRD (X-ray diffraction pattern).The data obtained from sintering was studied by the Bannister equation pattern and its dominant sintering mechanism was calculated. It was observed that the ZnO addition in $ZrO_2.MgO$ solid solution lead to increased zirconia stabilization .According to the vacancies model, the ZnO addition did not lead to zirconia phases stabilization (PSZ). An analysis of the rate control in the initial stage of the sintering showed a mechanism of volume diffusion type .in the other regions, the grain growth did lead to the Bannister equation deviation, which was observed by SEM (Scanning Electron Microscopy).these result were different from those demonstrate by other author who studied the $ZrO_2.Y_2O_3$ solid solution and obtained a mechanism of grain boundary diffusion.

3.1 Powder Synthesis

1. Dolomite stabilized zirconia powders were prepared by co-precipitation technique using 0.75mol/lit of zirconium oxychloride (AR Grade) solution and different type of dolomite viz. white, black, cream. Each of three dolomites about 3, 4, 5,6mol% of zirconia was solubilized with dilute HCL (1:1) to give a clear solution. Both the solutions were mixed and filtered if necessary. The calculated amount of the prepared solution was stirred and 1:1 vol.ratio NH_4OH was added slowly to that solution. Initial pH of the solution was 0.8-1.0 and on addition of cation increases slowly and a pH around 5-6 the gel gets more viscus. The gel was mechanically disrupted and further precipitation was carried out in the pH range 8.7-9.7 by the addition of AR quality NH_4OH (1:1). The precipitates were allowed to settle till a clear supernatant liquid was obtained. Subsequently the gel was washed with hot water till to free from chlorides and excess ammonia. The hydrated samples were oven dried and ground to fine powder. The phase evolution of calcined powder and sintered sample were studied by X-ray diffraction technique (Philips 1830, Netherland). The X-ray diffraction (XRD) patterns obtained from the calcined as well as sintered specimen were used to calculate the percentage of tetragonal ZrO_2 (X_t) in each composition by using the Equation below [23]

$$X_t = \frac{I_t(111)}{I_m(111) + I_t(111) + I_m(11\bar{1})} \times 100 \quad (1)$$

where $I(h\ k\ l)$ = intensity of (h k l) plane, m = monoclinic phase and t = tetragonal phase.

The powders were calcined at a temperature of 850⁰C with a holding time of 4 hrs in chamber furnace. The calcined powder was grinded by agate mortar. The calcined powder was mixed with 3%PVA solution and dried to fine powders. The binder added powder was uniaxially compacted at a pressure of 270MPa in cylindrical pellets (12mmΦ,3mm high) as well as rectangular bars (15mmX5mmX5mm) in a Hydraulic Press (10 T, SoilLab Testing Instruments,India). The non-isothermal densification behaviour of green compacts were studied with a dilatometer (NETZSCH 402C) at the heating rate of 5⁰C/minute upto 1400⁰C with alumina as reference material. The uniaxial pressing green compacts were sintered in air with a heating rate of 3^oc/min at the temperature range 1400⁰-1600⁰C with a holding time of 4 hours at the peak temperature. as well as sintered sample at temperature variation of 1400⁰C to 1600⁰C.The sintered density of the samples was measured by Archimedes's principle using kerosene as immersion liquid. The samples were polished using rotating disk and Automatic Grinding & Polishing Unit (Buehler, Ecomet 3-Automet 3). The hardness of the polished sintered samples was measured by Vickers Hardness Tester (Blue Star Limited, VM-50, India). The vicker hardness of the samples were calculated by using the following formula.

$$H_v = 1.854 \left(\frac{F}{D^2} \right) \dots\dots\dots(2)$$

F being the applied load measured in kgf

D is the half of the diagonal length of the indentation in mm.

The compressive strength of sintered samples was measured using UTM (Hounsfield H10KS, UK) by Brazilian Disc Test method. corresponding to each composition, a set of five samples was tested. The bending strength was calculated from the formula [24].

$$\sigma = \frac{2 P}{\pi D t} \quad (3)$$

where, P is the breaking load, D is the diameter of the pellet and t is the thickness of the pellet.

The samples were denoted as 3, 4, 5,6mol% white dolomite stabilized zirconia as xWDSZ, for cream xCDSZ and for black xBDSZ.(x =3-6 mol%)

3.3 Phase Evolution and Phase Stability Study

The powder was calcined at temperatures 850°C with a soaking time of 8 hrs in order to study the phase evolution of the powder. Phase stability of the compositions studied has been investigated from the X-ray diffraction (XRD) patterns of the samples sintered at different temperature range (1400°C to 1600 °C). The XRD was done using X-ray diffractometer (Model PW 1830, Philips, Holand). Cu $K\alpha_1$ radiation ($\lambda = 1.54056 \text{ \AA}$) was used as the incident X-ray beam at an accelerating voltage of 30 kV and a current of 25 mA. The powder samples were mounted on a flat XRD plate and scanned in the continuous scan mode (scan rate of $2\theta = 2^\circ \text{ min}^{-1}$) at room temperature in the range $20^\circ \leq 2\theta \leq 80^\circ$. The data obtained from the XRD was use to study the phase evolution of the stabilized zirconia with respect to different temperature.

3.4 Densification Study

Powder calcined at 850°C was mixed with 3 wt% PVA solution using an agate mortar. The PVA mixed powder was pressed into cylindrical pellet by conventional pressing technique. Pressing load was maintained at 270MPa.The green samples were sintered at different temperature range 1400°C to 1600 °C. The densities of the samples were measured by Archimedes's principle using kerosene as immersion liquid.

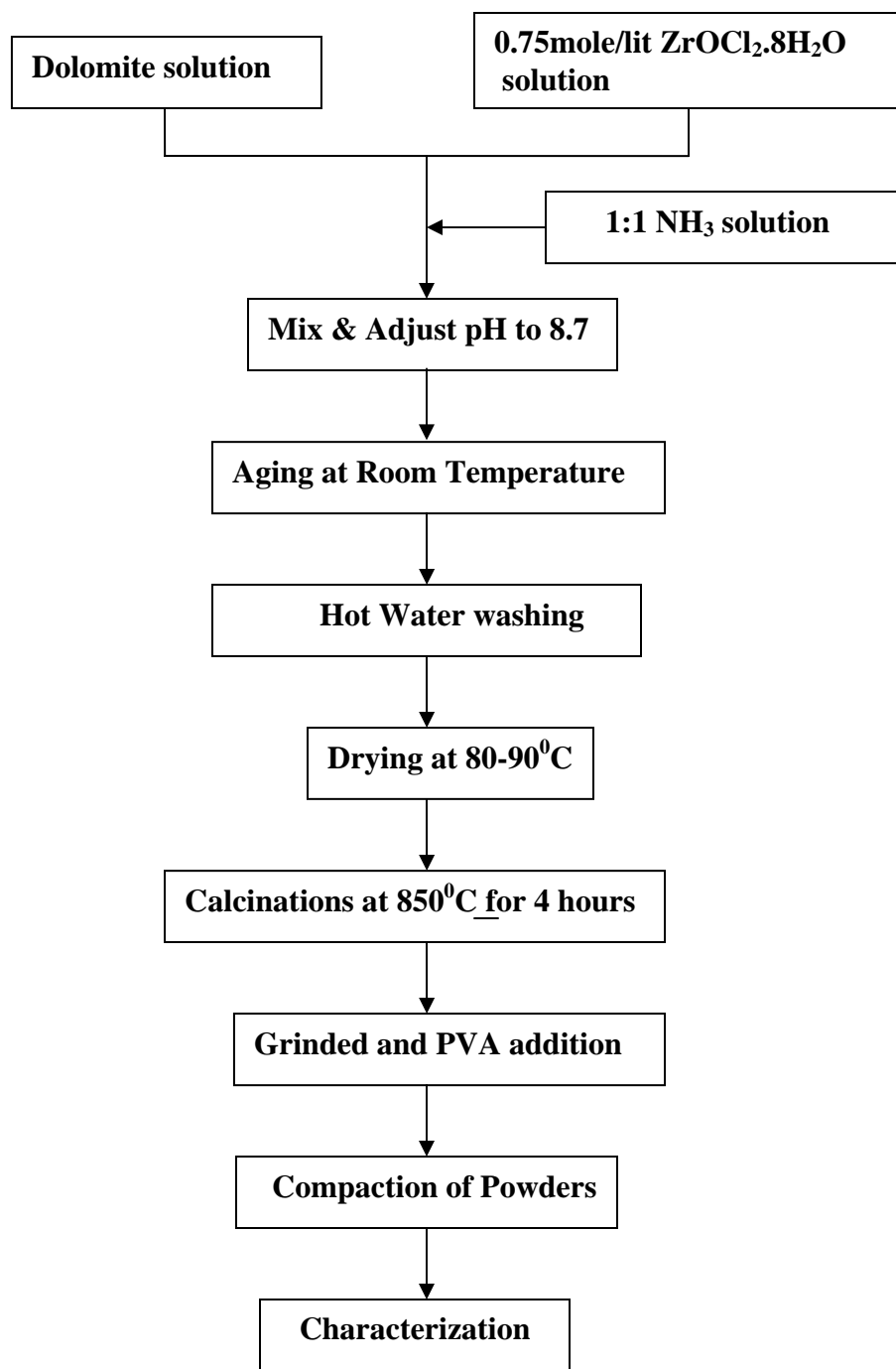


Fig. Flow diagram of powder synthesis by co-precipitation technique.

Phase Evolution

Phase evolution of dolomite stabilized zirconia system has been studied as a function calcination temperature and sintering temperature. The powder obtained after the synthesis co-precipitation process was calcined in the temperature 850°C for 4 hrs. The XRD pattern of the calcined powder samples were analysed for phase evolution. Characteristic XRD pattern for different type dolomite zirconia powders has been shown in Fig2 (a, b, c). The ‘as synthesized’ powders were found to be amorphous. The white dolomite stabilized zirconia powder shows purely monoclinic at lower composition which reduces on higher mole fraction of stabilizer. At 6% white dolomite the powders shows a combination of tetragonal and cubic phase with lower crystallite size.

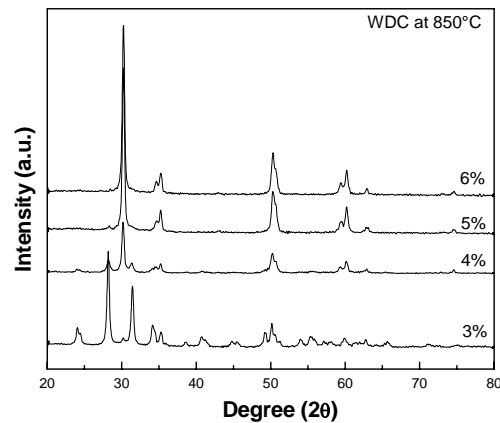


Fig.2(a): XRD pattern of the calcined zirconia mixed white dolomite as a function of different composition.

The Black dolomite stabilized zirconia having small amount of tetragonal phase at lower percentage(3mol%) but it will increasing with percentage of stabilizer .At higher percentage of stabilizer tetragonal percentage will be more. In comparison of white dolomite it has lower t-phase.

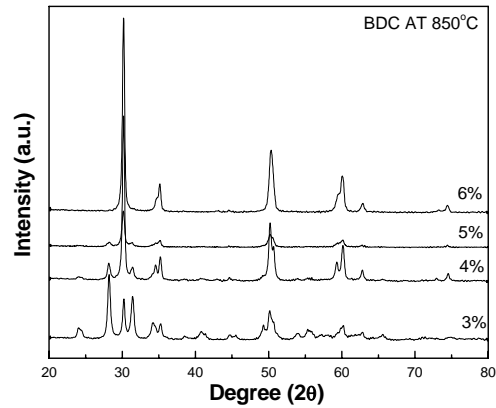


Fig.2 (b): XRD pattern of the calcined zirconia mixed black dolomite as a function of different composition.

In case of cream dolomite stabilized zirconia having more percentage of tetragonal phases than the other two at lower mol%, but the higher percentage of dolomite, white having better properties than other two.

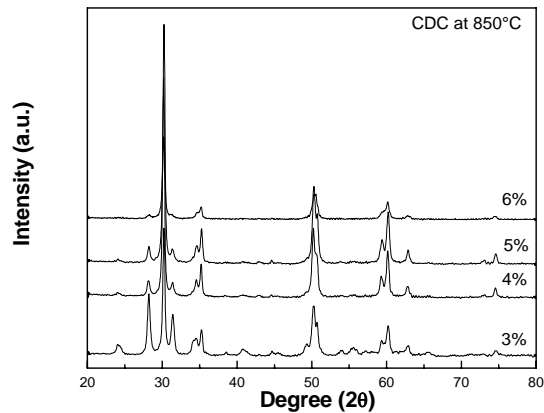


Fig.2(c): XRD pattern of the calcined zirconia mixed cream dolomite as a function of different composition.

Irrespective of different mol% of dolomite content “as synthesized” powder was found to crystallize in higher symmetry monoclinic phase at lower percentage but

increasing the percentage of stabilizer it will transform monoclinic to tetragonal phase at that calcine temperature .

The characteristic peaks of different composition were found broad at that both calcinations and sintering temperature and the sharpness of the peaks were found to increase with increasing the composition. This is due to the increase in crystallite size of the powders, which increases with increase in composition [26]. The sharp well defined peaks show the high crystalline nature of the synthesized phase without any impure phase.

Phase Stability

Characteristic XRD pattern of dolomite zirconia samples sintered at range of temperature 1400°C to 1600 °C is shown in Fig.3 (a, b,c, d). The sharp well defined peaks show the high crystalline nature of the synthesized phase without any impure phase. Thus the phases obtained remains stable even at high temperature sintering .This has been possible due to the very nature of the synthesis technique adopted in this investigation.

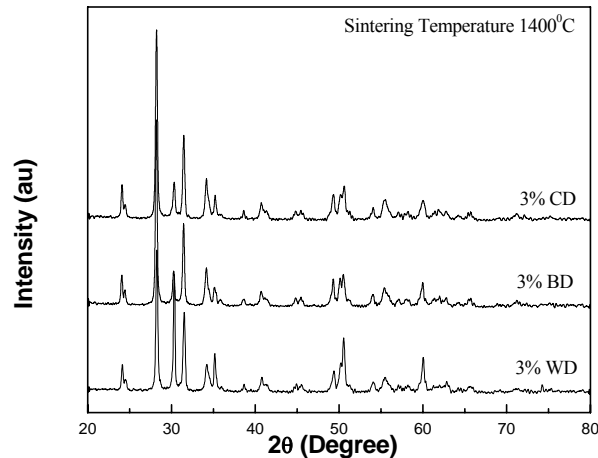


Fig.3 (a) XRD pattern of 3mol%dolomite mixed zirconia samples sintered at 1400°C.

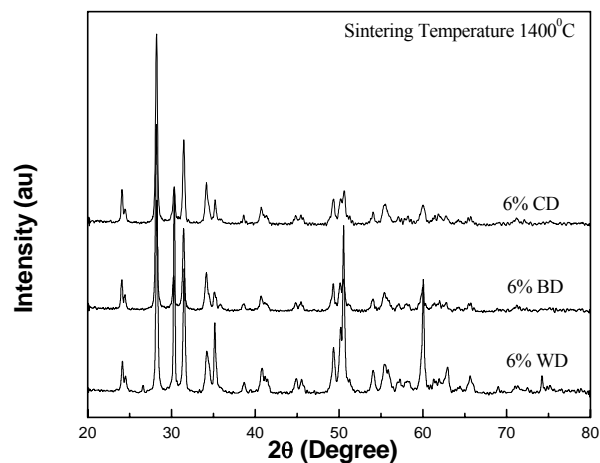


Fig.3 (b): XRD pattern of 6mol%dolomite mixed zirconia sintered at 1400 °C.

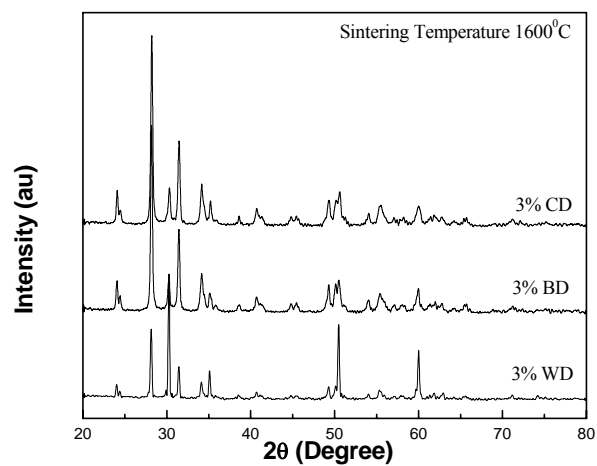


Fig.3 (c): XRD pattern of 3mol%dolomite mixed zirconia sintered at 1600 °C.

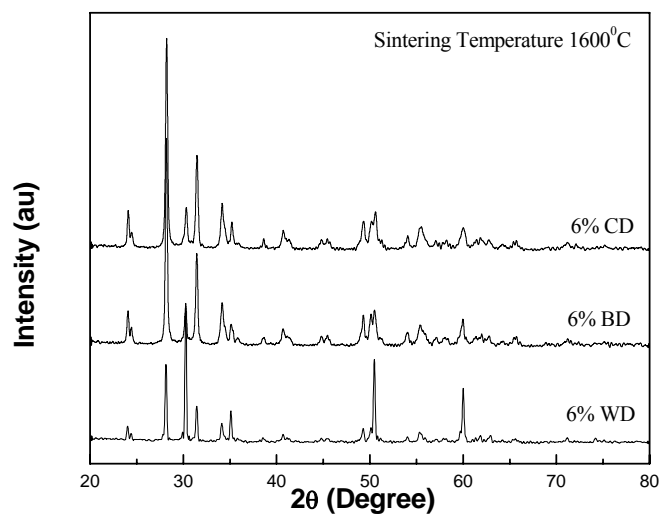


Fig.3 (d): XRD pattern of 6mol%dolomite mixed zirconia sintered at 1600 °C.

Densification Study

Density of the different composition variation and different type of dolomite mixed zirconia samples sintered at 1400°C to 1600 °C / 4 hrs has been shown in fig.4(a,b ,c,d) Density of the samples was found to increase with increasing dolomite content[27]. The white dolomite density variation to temperature 1400 to 1600 °C . Density is increasing with temperature. The density is higher at temperature 1550 °C and lowest in 1400 °C for all composition. After 1550 °C it will decrease drastically upto 1600 °C, due formation of micro cracks[28]. This is developing due to transformation of tetragonal to monoclinic or cubic phase.

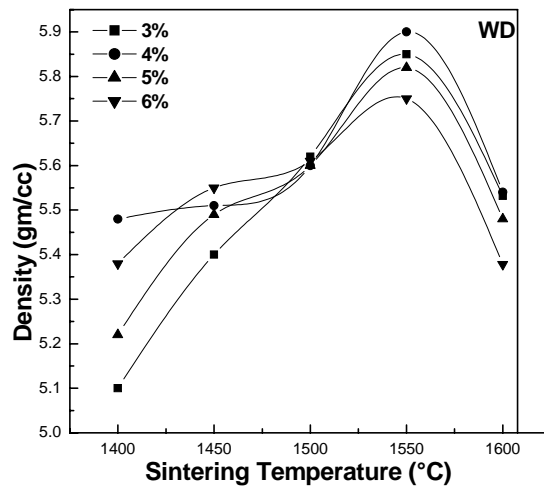


Fig.4 (a): density of white dolomite mixed zirconia at temperature 1400 to 1600 °C.

The black dolomite having better densification behavior than the white as well as cream dolomite .Density of black stabilized zirconia higher in 4%and lower in 6% shown in fig.4(b)

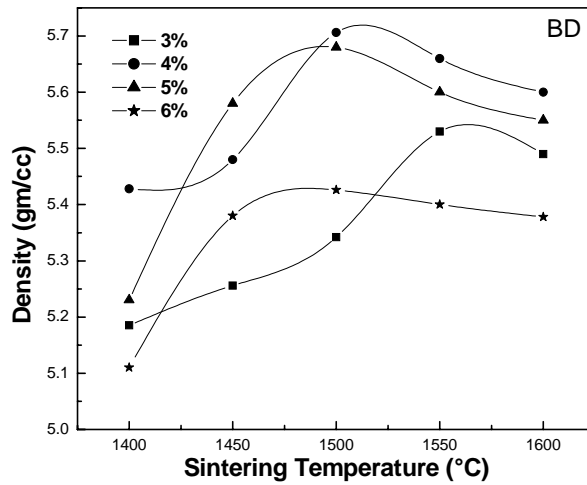


Fig.4 (b): density of black dolomite mixed zirconia at temperature 1400 to 1600 °C.

Density of cream dolomite increase in same manner like white dolomite in this case 6mo% having higher density and 3 mo% is lower one.

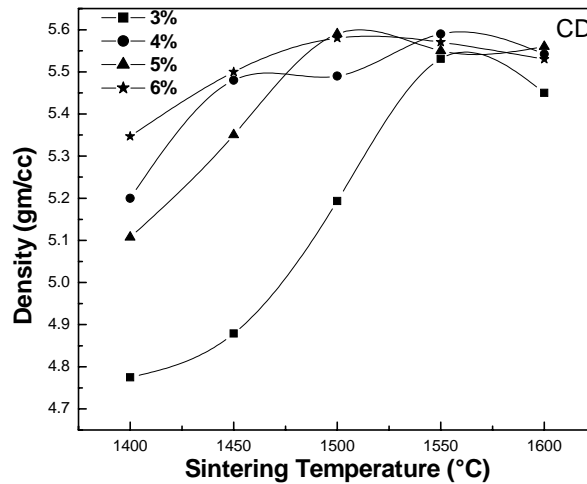


Fig.4 (c): Density of cream dolomite mixed zirconia at temperature 1400 to 1600 °C.

Relative density of different type of dolomite increasing in same manner .Lower relative density near about 80% in case of white dolomite .Black dolomite having higher relative density at lower temperature in comparison of other two dolomite .Relative density will

increasing with the temperature. At 1600 °C, all type of dolomite having higher relative density. The Black dolomite stabilized zirconia having 93.5% relative density.

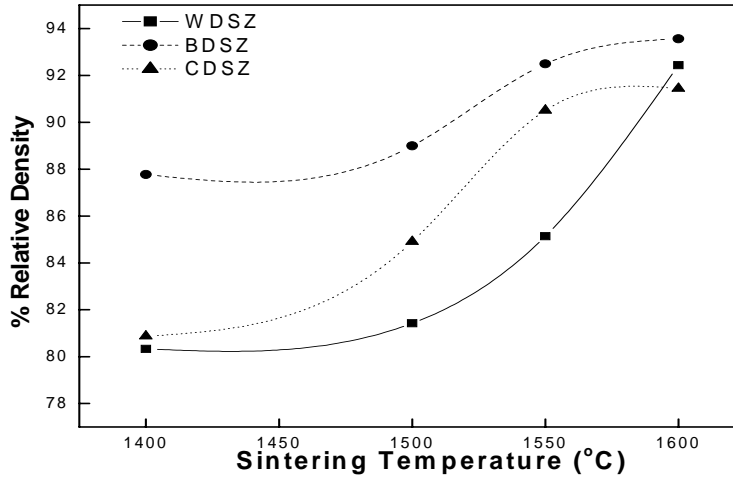


Fig.4 (d): Relative density as a function of sintering temperature

Bending Strength

The three point bending strength for dolomite stabilized zirconia was measured as a function of dolomite content (mol%) for both sintering temperatures of 1400°C and 1600°C. For both the temperatures, the strength decreased with increase in dolomite content with the maximum strength recorded for 4 mol% dolomite addition. However, the strength was more for 1400°C sintered samples and less for 1600°C sintered samples. This could be explained as follows: The grain size of dolomite stabilized zirconia is less at 1400°C which causes high density and small grain size. This results in higher strength at 1400°C. The grain size increases at 1600°C, which causes spontaneous t-m ZrO₂ transformation and results in microcrack formation. This decreases the strength. Further, among the three type of dolomite used, the black dolomite addition gave the highest strength, probably because of higher density, better stabilization.

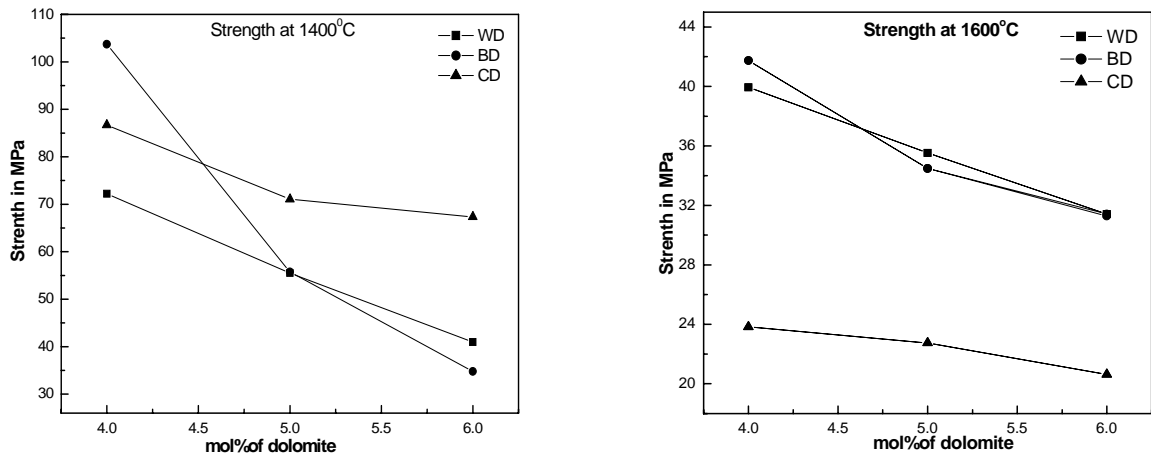


Fig.5: Bending Strength as a function of composition of dolomite

Hardness Test (Vickers hardness)

Hardness of the different type TZP sintered at different sintering temperature is shown in fig. Hardness of white dolomite is higher than the other two due to the higher relative density as well as higher t-ZrO₂ retention. The hardness decreases after reaching a maximum 10.8 GPa at 1550°C due to microcracks, though relative density is higher at higher temperature.

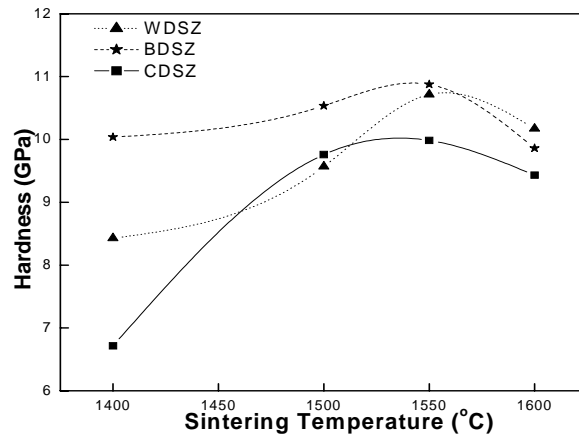


Fig.6: Hardness as a function of sintering temperature

5. Conclusions

Zirconia was stabilized using dolomite. It was observed that dolomite was a good stabilizer for PSZ formation. The effect of the type of dolomite was also studied. It was observed that black dolomite was best in terms of stabilization, strength and hardness. The significant improvement in hardness and strength value suggests that dolomite stabilized zirconia can be used commercially for producing strong and hard ceramic. The potential application areas as metal roller use in slurry compaction for paper mill, grinding media, nozzle for continuous casting of steel.

References

- [1] M.M. Schwartz, *Handbook of Structural Ceramics*, McGraw-Hill Inc, New York, 1992.
- [2] D.L. Porter, A.H. Heuer, Microstructural development in MgO–partially stabilized zirconia (Zr-PSZ), *J. Am. Ceram. Soc.* 63 (5) (1979) 219–224.
- [3] E. Mustafa, Microstructure and mechanical properties of PSZ toughened alumina ceramics prepared via polymeric sol–gel route, PhD thesis from Faculty of Science, Cairo University, May 1997.
- [4] S. Kumar, P. Pramamik, Innovative chemical method preparation of calcia stabilized zirconia powders, *Trans. J. Br. Ceram. Soc.* 94 (3) (1995) 123–126.
- [5] R.R. Hughan, R.H. Hannink, Precipitation during controlled cooling of magnesia partially stabilized zirconia, *J. Am. Ceram. Soc.* 69 (7) (1986) 556–563.
- [6] J. Luo, R. Stevens, Tetragonality of nanosized 3Y-TZP powders, *J. Am. Ceram. Soc.* 82 (7) (1999) 1922–1924.
- [7] S. Yin, S.U. Uchida, Y. Fujishio, M. Ohmori, T. Sato, Preparation of porous ceria doped tetragonal zirconia ceramics by capsule free hot isostatic pressing, *Trans. J. Br. Ceram. Soc.* 98 (1) (1999) 19–23.
- [8] W.D. Kingrey, H.K. Brown, D.R. Uhlmann, *Introduction to ceramics*, 2nd Edition, John Wiley and Sons, New York, 1976.
- [9] R.M. Dickerson, M.V. Swain, A.H. Heuer, Microstructural evolution in Ca-PSZ and the room-temperature instability of tetragonal zirconia, *J. Am. Ceram. Soc.* 70 (4) (1987) 214–220.
- [10] S. WU, R.J. Brook, Sintering additives for zirconia ceramics, *Trans. J. Br. Ceram. Soc.* 82 (1983) 260–264.
- [11] J.R. Hellmann, V.S. Stubican, Stable and metastable phase relations in the system ZrO_2 –CaO, *J. Am. Ceram. Soc.* 66 (4) (1983) 260.
- [12] S. Maschio, A. Trovarelli, Powder preparation and sintering behavior of zirconia–20 mol% ceria solid solution prepared by various methods, *Trans. J. Br. Ceram. Soc.* 94 (5) (1995) 191.
- [13] J. Saiki, K. Hirota, O. Yamaguchi, S. Inamura, H. Miyamoto, N. Shiokawa, K. Tsuji, Formation, Transformation and sintering of ZrO_2 –MgO compositions prepared from alkoxides, *Trans. J. Br. Ceram. Soc.* 92 (4) (1993) 161–164.

- [14] M.P. Pechini, US Patent 3, 330, 697, 1967.
- [15] M.A. Van De Graff, A.S. Burggraaf, Wet chemical preparation of zirconia powders: their microstructure and behaviors, in: N. Claussen (Ed.), *Advances in Ceramics, 12, Science and Technology of Zirconia II*, Am. Ceram. Soc., Columbus, OH, 1983, pp. 744–765.
- [16] E. Mustafa, Ca-PSZ prepared via polymeric sol–gel route, *Ceram. Int.* 26 (2) (2000) 215–220.
- [17] D.M. Ibrahim, E. El-Meliogy, Calcia stabilized tetragonal zirconia powders prepared by urea formaldehyde polymeric route, *Trans. J. Br. Ceram. Soc.* 99 (4) (2000) 159–163.
- [18] D.M. Ibrahim, E. El-Meliogy, MgO as a co-dopant for ceria partially stabilized zirconia, in: N.P. Bansal, J.P. Singh (Eds.), *Innovative Processing, Synthesis; Ceramics, Composites IV*, Am. Ceram. Soc. Conf. 102, 2000, pp. 341–349.
- [19] E. Mustafa, M. Wilhelm, W. Wruss, Microstructure and phase stability of Y-PSZ co-doped with MgO or CaO prepared via polymeric route, *Trans. J. Br. Ceram. Soc.* 101 (2) (2002) 1–5.
- [20] D.G.Lamas, R.E.Juhrez, A.Caneiru & E.Wakie deReca, *Nano structure Materials*, Vol. 10 7. (1998) 1199-1207.
- [21] Kandil, H. M., Greiner, J. D. & Smith, J. F., *J. Am. Cer. Soc.* 67 (I 984) 341.
- [22] E.C. Subbarao, H.S. Maiti, *Solid State Ionics* 11 (1984) 317.
- [23] Becher, P. F., Swain, M. V. & Ferber, M. K. *J. Mat. Sci.*, 22(1987) 76.
- [24] S.K. Durrani , J. Akhtar , M. Ahmad, M.A. Hussain 100 (2006) 324–328
- [25] Lange, F. F., Vol. 4, Plenum Press, New York, 1978, p. 799.
- [26] D. G. Jensen, *Jor. of the Euro. Ceram. Soc.* 16 (1996) 825-831.
- [27] C.Chung, T. Yang, Wen-Cheng J. Wei *Wear* 242 (2000).97–104
- [28] Green D. J., Hannink, R. H. J. & Swain, M. V., CRC Press, Boca Raton, FL, 1989.