

Electric Field Assisted Sintering of Metal Oxides

by

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Cover:
[Difference between conventional sintering and field assisted sintering]

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This thesis is dedicated to my loving parents

SUMMARY

Electric field assisted sintering techniques, FAST or FLASH have become the novel research fields for the past few years. One of the primary reasons for the rise is the potential benefits which these techniques have brought. The chief benefit is the reduction in the sintering time and temperature, which is very important in terms of energy savings and low production cost. How the electric field enhances the sintering rate is still not fully understood. However, it is believed that electric field halts grain growth which indirectly increases the sintering rate. Joule heating at grain boundaries is another decisive factor in increasing sintering rate by simultaneously increasing the diffusion at grain boundaries and lowering the driving force for grain growth. In this thesis, electric field influence with respect to microstructure, mechanical properties and sintering temperature required for densification is being studied. The materials studied are; yttria-stabilized zirconia, ceria-stabilized zirconia and titanium oxide. It is found that electric current rather than electric field is the main variable which controls the densification rate. Electric field or voltage only governs the conduction behavior due to the dielectric properties of metal oxides. Densification rate is directly proportional to current density and current intensity. Thus by carefully controlling these parameters the onset of FLASH sintering can be controlled. It is also found that application of electric current at higher densification temperature increases grain growth than normal sintering. Microstructure analysis and sample internal temperature measurements showed that Joule Heating, grain growth retardation and increased ionic mobility are the main causes of increased densification rate.

Keywords: Electric field assisted sintering, yttria-stabilized zirconia, ceria-stabilized zirconia, titanium oxide, electric current, joule heating

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Important Notations

ρ	Density
σ	Stress
μ	Chemical Potential
V	Voltage
I	Current
R	Resistance
G	Gibbs free energy
Y ₂ O ₃	Yttrium oxide
ZrO ₂	Zirconium dioxide
CeO ₂	Cerium dioxide
Al ₂ O ₃	Aluminum Oxide
TiO ₂	Titanium Oxide
R ₁ and R ₂	Principal Radii of curvature for the surface
E_m	Migration Energy
Y'_{Zr}	Y in the Zr site with negative charge
$\ddot{V}_O$	Vacancy in the oxygen site with the double positive charge
O^x_O	Oxygen in the lattice with net zero charge
γ_w	Interfacial Energy
ΔH_w	Excess Enthalpy
ΔS_w	Excess Entropy

Chapter One

Introduction

1.1 Overview

Sintering, in most cases is the final stage in processing of ceramics, hence it has a great influence on the intrinsic and extrinsic properties of ceramic powder compact. It transforms 'green body' powder compacts into dense ceramic components by the application of high temperature and sometime also a high pressure [1]. In practice, sintering is controlling of both the densification and grain growth. Since densification requires high temperatures, grain growth naturally occurs during sintering. Repression of this parameter has key importance in engineering ceramics. [2]

Electric field assisted sintering techniques; FLASH and FAST, have been gaining attentions as new methods of consolidation. The inherent benefits of these techniques are reduced sintering temperatures, overall cycle time reduction and reduced grain growth which is very important in view of some metal oxides. [3]

The concept of applying an electric current was first used by Taylor in 1930 [4]. But this idea was not fully utilized until the arrival of first commercially available spark plasma sintering machine in the early 1990's. In Spark-Plasma Sintering the powder compacts are densified by the application of external pressure plus internal heating [3]. Later in 1990's different papers were published on spark plasma sintering claiming reduction in sintering time and temperature [3]. But none explained the exact mechanism behind it. Some thinks it is this internal heating caused by electric current which is responsible for the reduction in sintering time and some relates it to the electric field effects [2,6,7]. In literature, this technique has been called by many names like, Field Assisted Sintering (FAST), Spark Plasma Sintering (SPS), Pulsed Electric Current Sintering (PECS) and Plasma Assisted Sintering (PAS). [3]

Sintering rates are sensitive to grain size [2]. Reduction in grain growth can thus enhance the sinterability. It was shown by U. Anselmi-Tamburini et al. that lower grain size in the case of SPS was obtained [5]. Ghosh et al. conclusively showed that by the application of a weak dc electric field grain growth in yttria stabilized zirconia can be significantly reduced [6]. Rishi raj et al. later revealed that sintering rate in the case of yttria stabilized zirconia can be enhanced by the application of a weak dc electric field. They concluded that the enhanced sintering rate is due to the retardation in grain growth

by the application of electric field [2]. Ghosh et al. further explained this phenomenon and related it to space-charge defect chemistry disruption due to electric field. They also explained the effect of joule heating on grain growth [6]. Cologna et al. took a step further and found that yttria-stabilized zirconia can be sintered to full density in just few seconds at around 850°C. They called it FLASH sintering and indicated that field strengths of above 40V/cm were necessary for it to occur. They explained their findings in terms of local joule heating and presented a hypothesis that the local joule heating at grain boundaries increases the grain boundary diffusion, while simultaneously halting grain growth [7].

All the above stated findings are based on the basic hypothesis that electric field retards grain growth. Though there are enough results of retardation in grain growth when subjected to the electric field, but an assistive theory is yet to be presented. Also, there is no data regarding the micro-structural and mechanical effects of applied electric field.

The motivation of this work is to study the influence of external field on the sintering and how this influence the material with respect to microstructure, mechanical properties and sintering temperature required for densification, as the current research is only limited to reducing the sintering temperature. Extensive study of the causes of increased densification rate is also the part of this thesis. Currently research has been carried out only on a ceramic with ionic conductivity, yttria-stabilized zirconia. But does the electric field have the same affect on insulating ceramics? In this thesis, both ceramics with ionic conduction and with no conduction are being evaluated.

1.2 Basic Theory

1.2.1 Stabilizer's effect

Partially stabilized tetragonal zirconia is very important engineering ceramic. The most important benefit of this partially stabilized phase is the increased fracture toughness. This is governed by a mechanism known as transformation toughening [8].

Pure zirconia has a monoclinic crystal form at room temperature. The tetragonal form is stable at around 1000°C-1100°C, thus stabilizers are added to retain this tetragonal phase at room temperature [1]. By carefully controlling the stabilizer composition, heat treatment cycle and cooling rate this tetragonal phase can be retained in individual grains [1].

Different cationic dopants, e.g. CaO, Y₂O₃ and CeO₂ are act as stabilizers [8]. These dopants are used to stabilize the tetragonal phase at room temperature. Metastable tetragonal zirconia increases the fracture toughness of zirconia materials. At the same time the cationic dopants produce necessary oxygen vacancies for the ionic conduction of zirconia. With an excessive addition of stabilizers, a fully stabilized cubic phase would be obtained at room temperature, which does not contribute to an increase of the fracture toughness [1].

1.2.2 Densification behavior in metal oxides and forces behind it

Densification of ceramic powders in the solid state is considered to be a two stage process [9]. In the initial stage of densification, the individual powder particles are recognizable and the porosity between the particles is interconnected *Figure 1*. In equation form, ($D_0 < D < 0.9$), whereas D_0 is initial packing relative density and D is the relative density [9]. The initial stage of densification can be further divided into two phases; one is related to the rapid growth of the interparticle neck with no substantial shrinkage or densification. In the second phase (also referred as intermediate stage of sintering), pore structure becomes smoother, and interconnectivity emerges in a cylindrical fashion [10]. This phase is characterized by the highest shrinkage rate of the compact. Grain growth also occurs in the later portion of this phase, so without any doubt this phase is the most important one in determining the properties of compact [10].

During the final stage, the pores are constricted, inter connectivity vanishes, giving discrete pores ($0.9 < D < 1$). Densification at this stage is due to the shrinkage of closed pores [9].

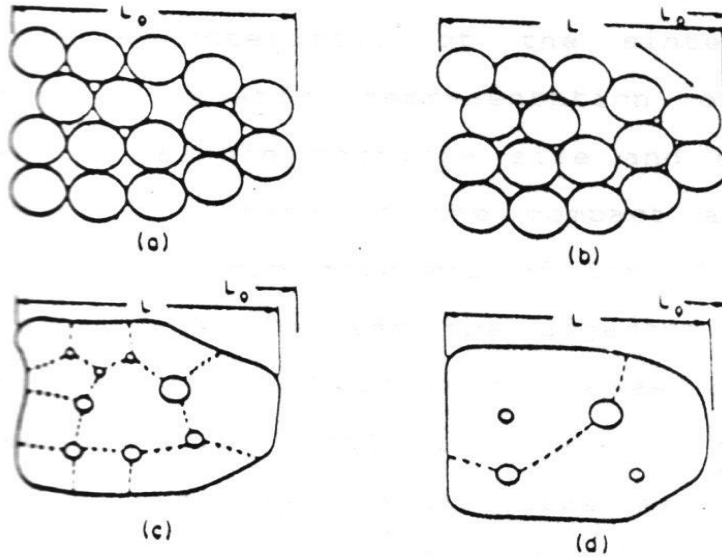


Figure 1: Schematic Representation of Densification stages (a) Powder Compact (Aggregates) with particles and interconnected porosity (b) Initial Sintering with neck formation (c) intermediate stage (d) Maximum Densification [11]

During densification of a metal oxide several material transport mechanisms may be active, like surface diffusion, vapor transport, boundary diffusion and lattice diffusion, all of which lead to the reduction in surface energy [12]. Surface diffusion and vapor transport are surface transport mechanisms and mainly related to particle coarsening. They promote the neck growth between the particles without increasing the density of the compact as only particle surfaces are involved [12]. Density is increased by the bulk transport mechanisms which include lattice (volume) diffusion, boundary diffusion, plastic flow and viscous flow. They remove material from inside the particle and deposit it at the neck [10]. Depending on the type of material being sintered, one or couple of these mechanisms may be active during the sintering [10].

Reduction in surface energy concept is fair enough during the initial stage of densification, but in the latter stages there are some other factors too which governs the densification. According to German, stress associated with a curved surface is: [10]

$$\sigma = Y(R_1^{-1} + R_2^{-1}) \quad (1.1)$$

Where, Y is the surface tension, R_1 and R_2 are the principal radii of curvature for the surface. For the concave surfaces negative sign is used for R because of the morphology that radius is located inside the mass. With the help of equation (1.1), stress value at the neck can be calculated [10].

At a small distance away from the neck along the surface, the curvature is constant with both R_1 and R_2 are equal to the sphere radius $D/2$, as shown in the *Figure 2*, hence;

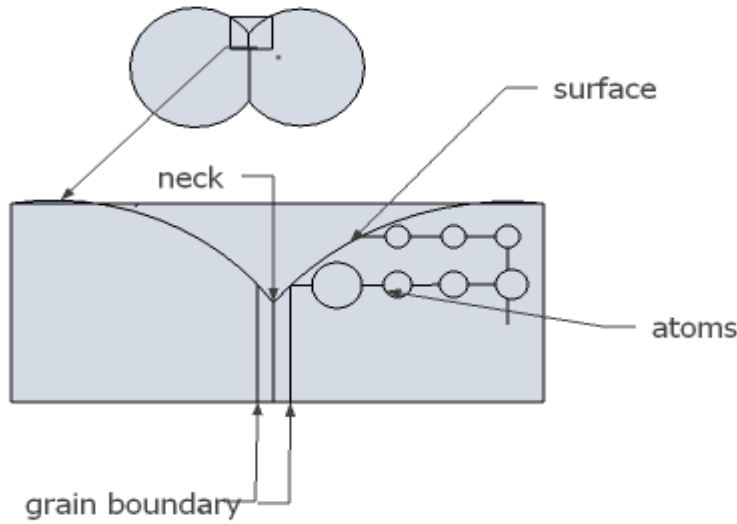


Figure 2: Atomic view of two particles when neck has formed. Misalignment between atomic bonds of two particles results in grain boundary. (Not shown here) Neck region is the region of highly disrupted atomic bonds [10].

$$\sigma = 4Y/D \quad (1.2)$$

Where, Y is the surface tension and D is the sphere diameter.

Now assuming the circle approximation of neck, the stress at the neck;

$$\sigma = Y\left(\frac{1}{x} - \frac{D}{x^2}\right) \quad (1.3)$$

This difference between equation (1.2) and (1.3) depicts that there is a large stress gradient in the neck region. This stress gradient provides the driving force for diffusion. In general, the interparticle pores provide this curvature gradient at every stage of sintering, which is highest in the intermediate stage, that's why this stage contributes the most in the densification process. As contact between particles grow this stress or curvature gradient is annealed out, slowing the process in the last portion of intermediate stage and in the final stage of sintering [10].

In the intermediate stage of densification when grain boundaries have formed, they play their part in increasing densification by effective and fast diffusion along the dislocation paths. These dislocations increase diffusion by lowering ΔG for migration.

1.2.3 Ionic Conduction in Y_2O_3 - ZrO_2

The ionic conduction of yttria stabilized zirconia is due to the diffusing oxygen ions [14]. Oxygen ions move around in the lattice by vacancies riding as shown in the Figure 3 below:

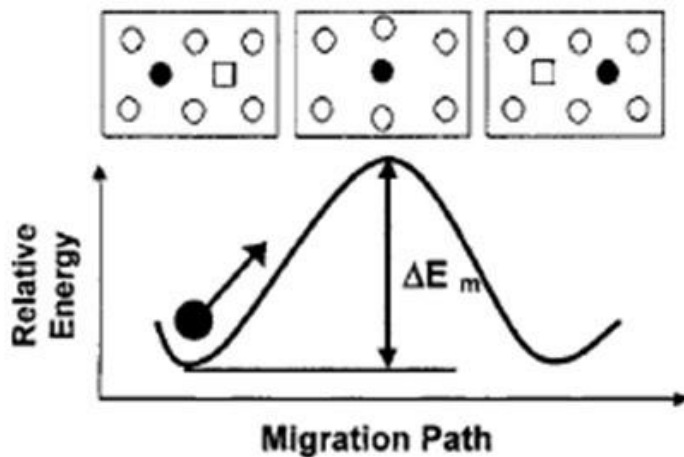


Figure 3: Oxygen ion diffusion in the lattice by the simultaneous creation and destruction of vacancies. The Migration energy ΔE_m is provided by the temperature [16,27]

These vacancies are produced when zirconium ion (Zr^{4+}) is replaced by low valent cations (e.g., Ca^{2+} , Mg^{2+} , Y^{3+}). This substitution gives rise to the net negative charge in the lattice and to keep the charge neutrality condition, Oxygen vacancy is formed accordingly, in Kroger-Vink notation;



Where Y'_{Zr} means Y in the Zr site with negative charge, $\bar{V}_O$ is the vacancy in the oxygen site with the double positive charge and O^x_O is the oxygen in the lattice with net zero charge [18].

1.2.4 Joule Heating

When electric current flows through a resistor some of the electrical energy is converted into heat. This process is called as Joule Heating, first observed by James Prescott Joule. The power or heat released in this process is equal to both the current flowing through the resistor and the voltage drop across the resistor [21].

$$Q = VI \quad (1.5)$$

Or, as $V=IR$

$$Q = I^2 R \quad (1.6)$$

For the same current flow, the high value resistor dissipates more heat.

1.2.5 Spray-Freeze Granulation

Granulation process prior to powder pressing is very important in order to obtain free flowing granulates that evenly fill the pressing die and facilitate the following compaction of the green bodies [20]. Granulation starts with the initial mixing of binder, plasticizer and starting powder in water to make a suspension. The percentages of binder and plasticizer to be used depend on the respective ceramic powder properties. This suspension is then used to make granulates [20].

The two most common and widely used methods to make granulates are spray drying and freeze drying. In spray drying the suspension is sprayed and dried in hot air. Using hot air as drying medium has some drawbacks. The most common of them is the hardening of granulates due to the binder segregation around the periphery [20]. Freeze drying, on the other hand uses liquid nitrogen as a freezing medium. It is a two step process. First, suspension is sprayed into liquid nitrogen. The droplets are immediately frozen, *Figure 4*. In the second step these frozen droplets or granules are subsequently dried by lyophilisation which involves sublimation of ice [22]. As no liquid phase is involved, freeze drying produces spherical, free flowing granulates with homogeneous distribution of binder.

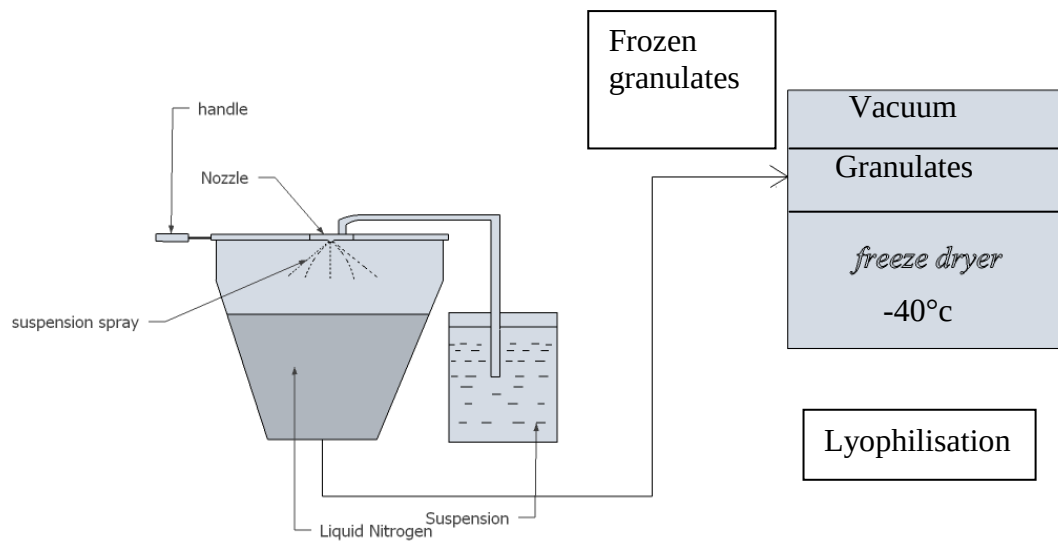


Figure 4: Spray-freeze drying process

Chapter Two

Experimental Background

2.1 Procedure

The tetragonal zirconia powder (Tosoh TZ3YSE, Japan) used contained 3 mol percent of Ytria as a stabilizer.

The same procedure was carried out for $\text{CeO}_2\text{-ZrO}_2$ powder containing 12 mol % of CeO_2 and TiO_2 powder. But for TiO_2 , first its powder was produced by spray-freeze granulation.

Discs were prepared by using 3 grams of powder. The powder was pre pressed uni-axially at 6 MPa to make blanks for Cold Isotactic Pressing (CIP). These blank were then placed in balloons and CIP at 300 MPa. The balloons acted as blank handlers and also as rubber diaphragms for cold isotactic pressing (CIP). See the schematic illustration in figure 5 below;

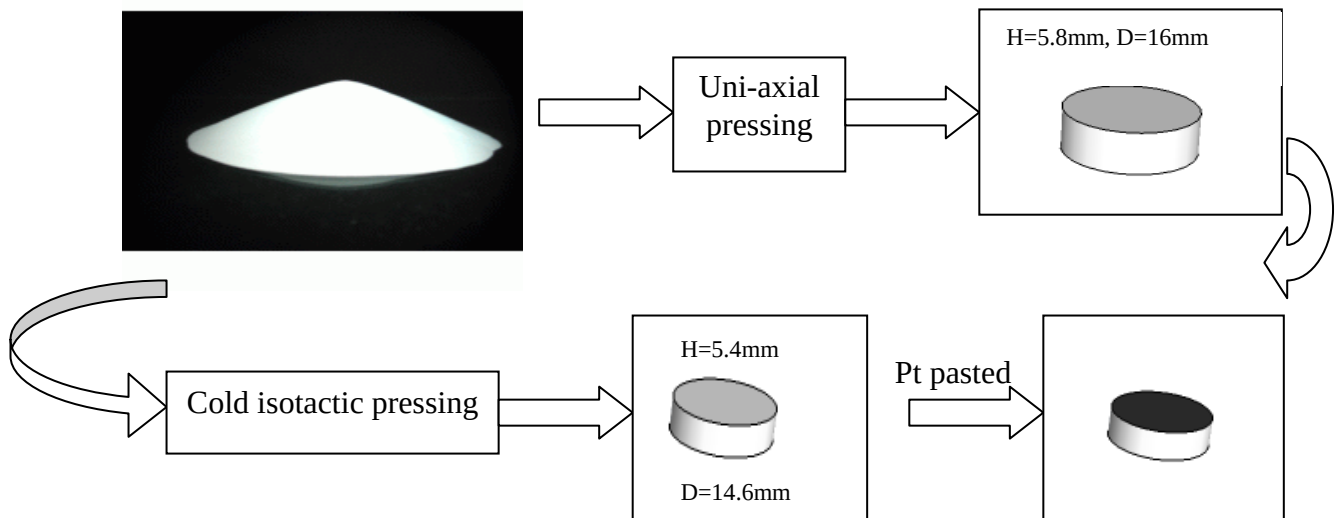


Figure 5: Schematic diagram explicitly explaining the zirconia discs formation.

The green density of the CIP discs were calculated and found to be around 50% of the theoretical density. Sintering procedure was carried with and without electric field. When the sintering procedure was performed with an electric field, the discs were coated with platinum paste on both sides in order to eliminate the uneven current distribution over the surface. Platinum paste makes the whole surface conducting. If it is not applied then current density will be high at some spots and low on others, leading to current density fluctuations within the disc, i.e. higher current density areas will be more

densified compared to low current density areas, spawning cracks and eventually fracture. The complete experimental setup is shown in the *Figure 6*.

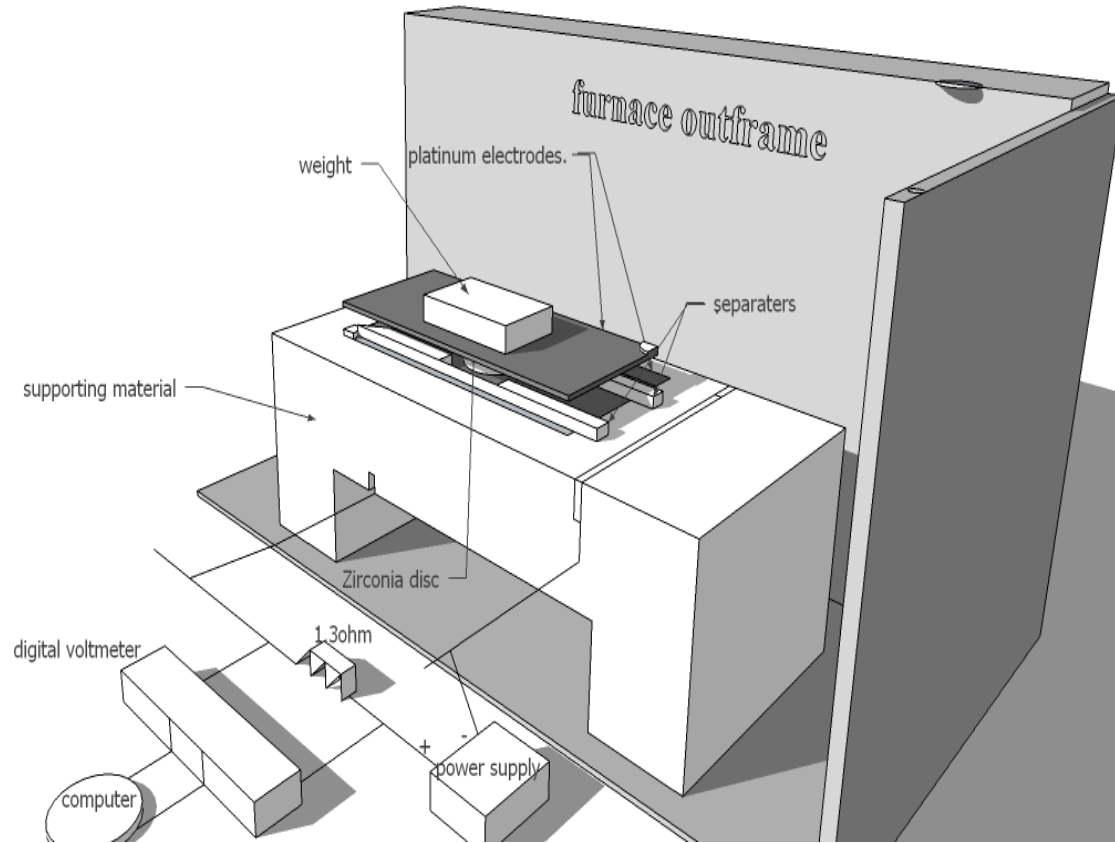


Figure 6: Experimental Setup

The zirconia discs were placed between two platinum electrodes, which were attached to a power supply (max. 60V(dc)/1A). Two separator rods were also placed in-between the platinum electrode to diminish the risk of short circuiting and to ensure a uniform contact between the electrodes and the disc a small weight of $\approx 15\text{g}$ was placed on the upper platinum electrode. This whole assembly was placed on a supporting refractory material.

To the circuit, a resistance of $1.3\ \Omega$ was attached in a series. The current through the sample was then calculated from the voltage drop across the resistance. The voltage drop was measured every 60s with a digital multi meter connected to a computer.

2.2 Spray-Freeze Granulation of TiO₂ Suspension

TiO₂ suspension was made according to the recipe given in Table (see appendix A).

The suspension was granulated by spray freezing with the help of liquid nitrogen. The ice in the frozen granules was removed by freeze drying.

Different sintering temperatures were selected and the sintered density was measured. As shown in the table (see appendix B)

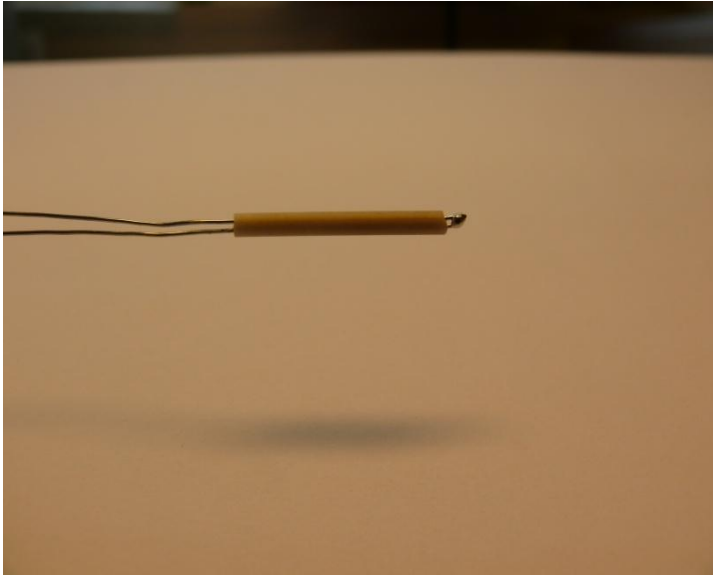
2.3 Mechanical Testing of CeO₂-ZrO₂

Biaxial flexural testing was carried out on two sets of samples; conventionally sintering set (5 samples) and field assisted sintering set (6 samples) using the standard procedure (see appendix C). The sintering temperature for the materials used was 1300°C in case of field assisted sintering and 1350°C for conventional sintering. The selected sintering temperatures were selected in order to obtain the same density of 96% for both materials.

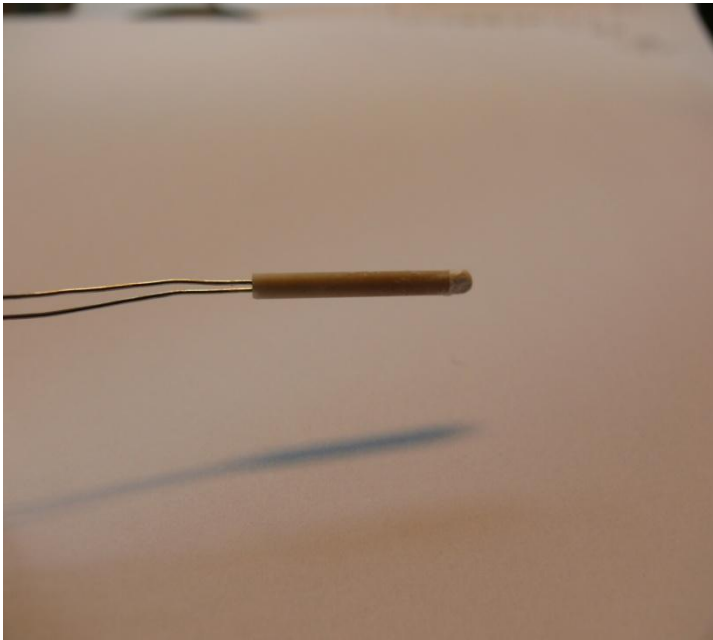
2.4 For measuring Joule Heating Effect

The local heating of sample was measured using a thermocouple (*Figure 7a*) inserted inside the sample center by a drilled hole, in order to record temperature within the sample compared to the surroundings. To protect the wires from conducting while inside the sample, the joint was coated with the Al₂O₃ paste (*Figure 7b*) and to keep them separated Al₂O₃ tubes were used.

The complete sub-assembly for measuring internal temperature of the sample is shown in *Figure 8*. A hole with a diameter of 2mm was drilled from the side of the disc. The hole was drilled to a depth slightly deeper than the radius of the disc to allow the thermocouple to be placed in the center. The Al-oxide tube used as a separator had a diameter of 1.7mm, which allowed the sintering shrinkage to occur. The temperature measurements from the thermo couple inside the sample was recorded every 60s.



a) Platinum wires welded from one side and held separated by Al_2O_3 tube.



b) The joint was coated with the Al_2O_3 to prevent conduction

Figure 7: Thermocouple wire assembly

Figure 8 Illustrates the complete sub assembly and important parameters.

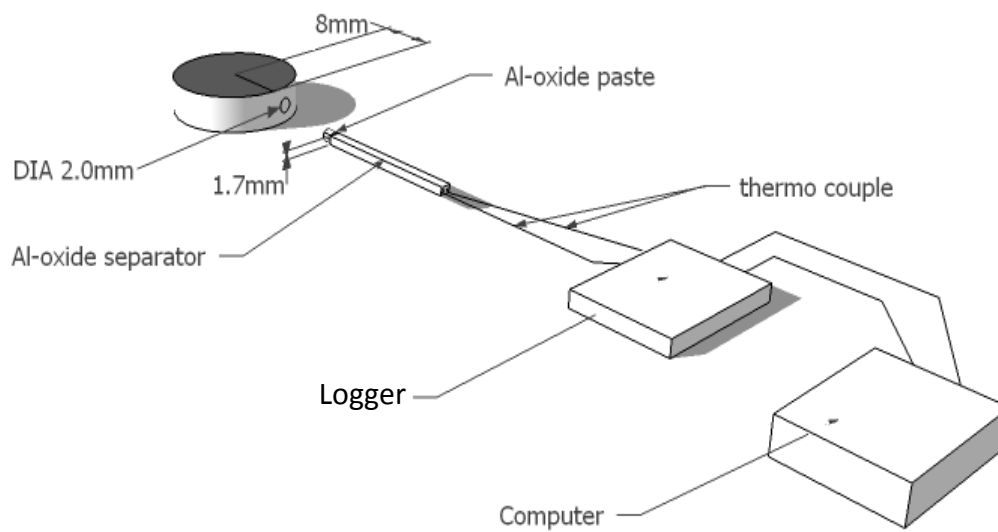


Figure 8: The complete sub assembly for measuring internal temperature of the sample. Drill depth was selected as 8mm, little bit higher than the actual value (7.3mm) for accurate measurements. The interval for reading the thermocouple was selected as 60s to integrate with the original experimental set up.

Chapter Three

Results and Discussions

3.1 Comparison between two Sintering Scenarios

The main result of this thesis work is shown below in *Figure 9 and 10*.

The sintering temperature needed to reach a particular density was reduced when field assisted sintering was used compared to conventional sintering where no electric field was used (*Figure 9*). As an example, when sintered at 1150°C, TZP-3Y reached a density of 57.5% without an electric field and when an electric field was applied, the density was increased to 73.3%. The electric field can thus be used to influence the densification i.e., higher density can be reached at lower temperatures. When field assisted sintering was used as shown in *Figure 9*, a density of 96% could be obtained at a temperature 100°C below what otherwise would have been required.

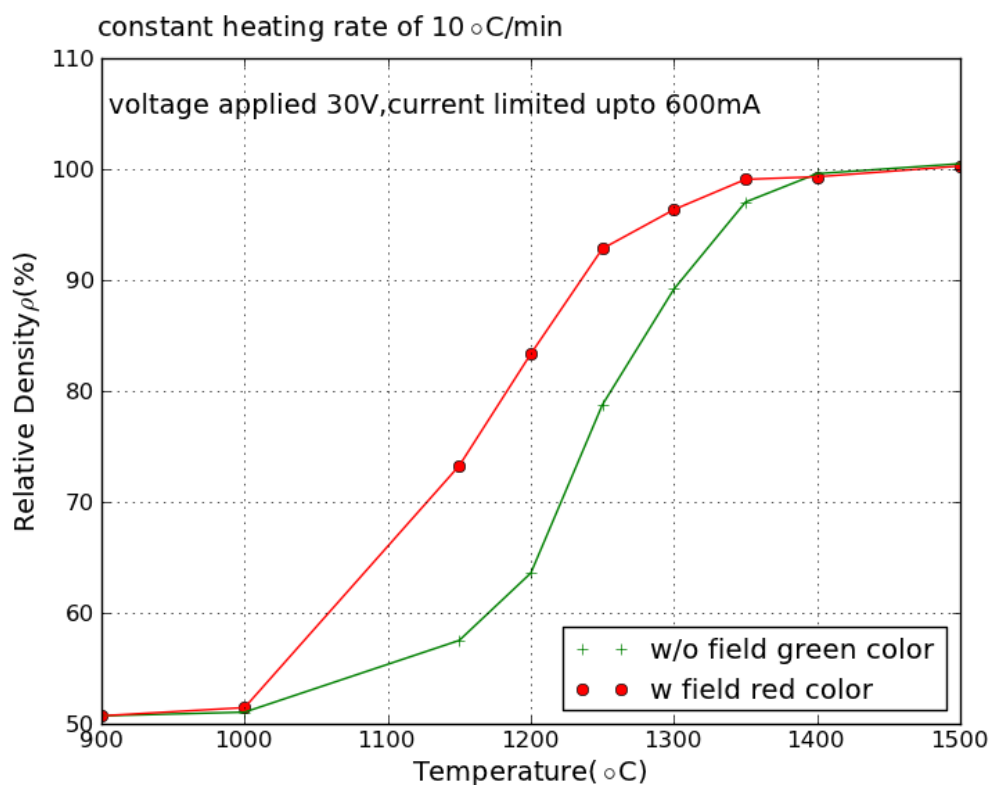


Figure 9: Relative density as a function of temperature when the materials were sintered with and without an electric field.

When an electric field of 30V was applied across the TZ-3Y material and the temperature was increased by 10C°/min, conduction of current at room temperature

through the isolating material was initiated when the temperature reached around 620°C. The conduction increased with temperature as shown in *Figure 10* and at around 920°C the specified value of 600mA generated by the power supply was reached. During the cooling cycle, the conduction remained at 600mA until the furnace temperature was around 700 °C where it suddenly dropped.

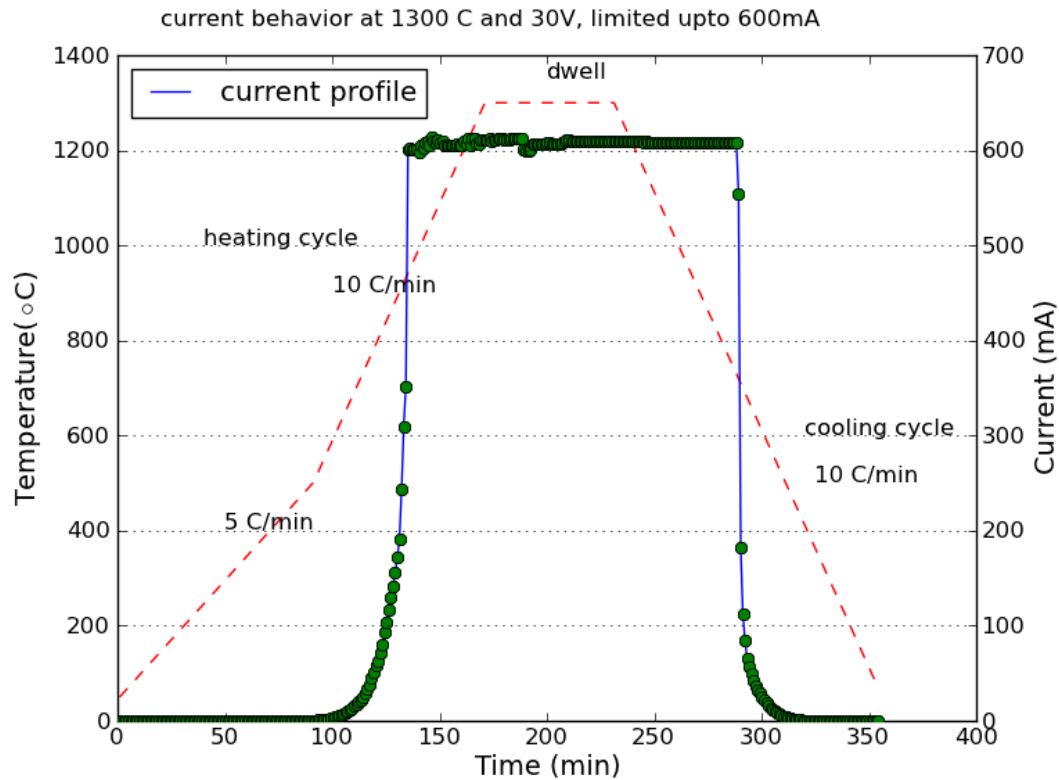


Figure 10: Conduction behavior of yttria-stabilized zirconia at 30v.

Densification in yttria-stabilized zirconia is generally governed by lattice and grain boundary diffusion [13], both long range and short range diffusion are likely to take place. The rate controlling species in the densification process of yttria-stabilized zirconia are cationic interstitial, which are in this case Zr and Y atoms. Oxygen vacancies are highly mobile, and for densification rate, slow diffusing species are more important than highly diffusive species [13].

Referring to *Figure 9*, it is clear that at low temperatures, at and below 900°C the densification was not influenced by the electric field for the conditions studied. It can be deduced that electric field does not influence the density at the initial stage of sintering. This was due to the relatively porous structure where the contact area between the particles was small, which results in a high resistance. The current at low temperatures

was thus not sufficient to significantly enhance the material transport required for the initial sintering. However, as temperature increases above 900°C, the contact area increases and leads to an increased conduction at the end of the initial stage.

The largest shrinkage occurred in the temperature range of 1100°C to 1300°C and can be assumed to represent the intermediate stage sintering as discussed above. In this region there was also a significant difference between the sintered densities when the sintering was performed with or without an applied field (*Figure 9*). From *Figure 10* this range lies in the maximum conduction range and indicates that the electric current readily affects the intermediate stage of densification. See *Figure 11*.

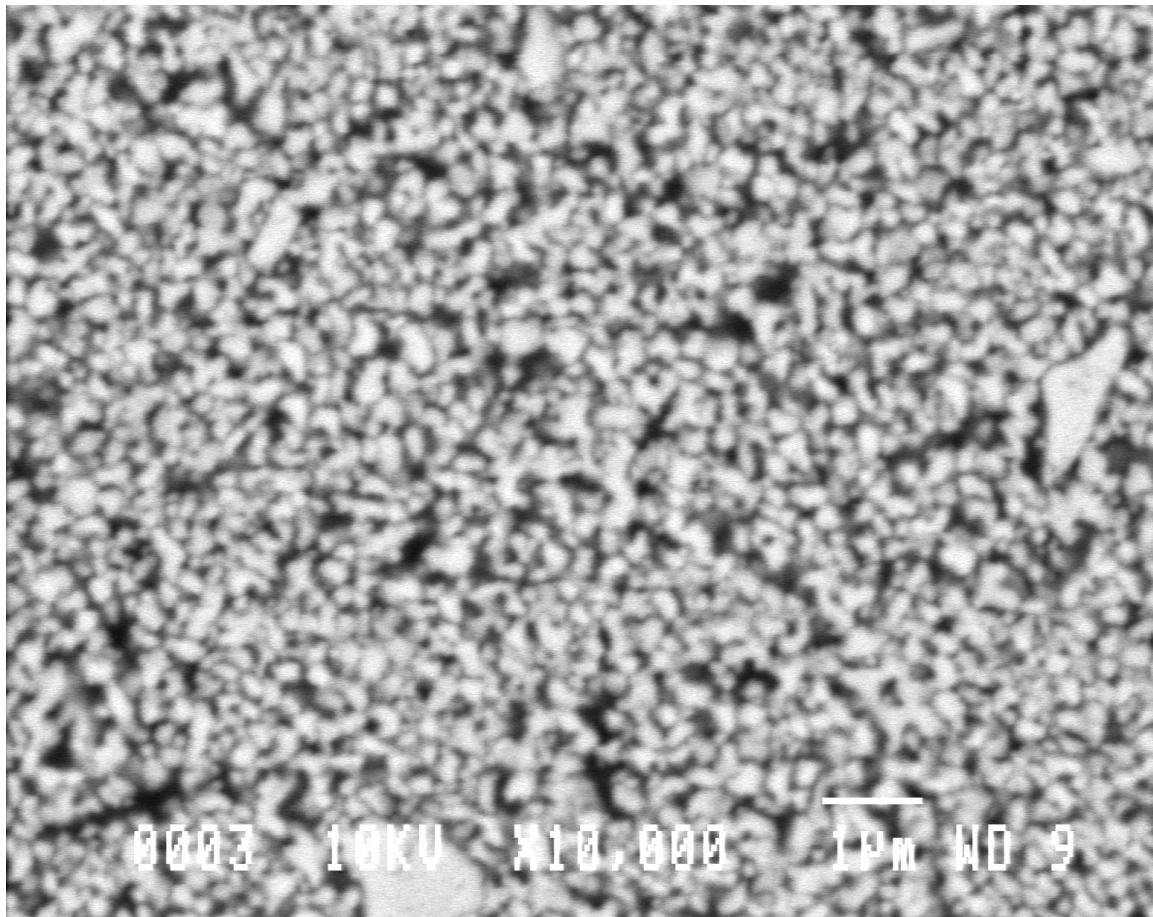


Figure 11a) Sintering temperature 900°C. Micrographs for both scenarios were same, only one is shown here. The structure is highly porous and few powder agglomerates are also present.

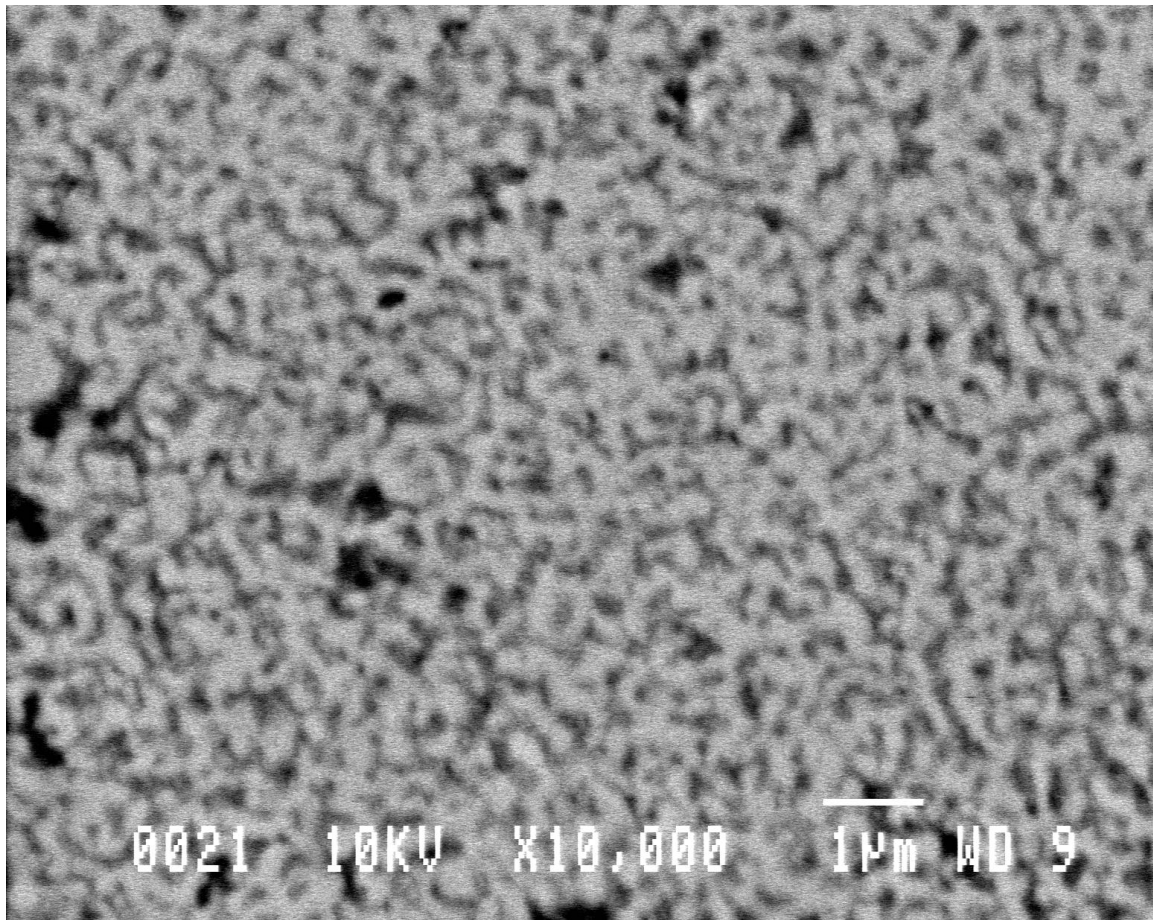


Figure 11b) Sintered at 1200°C without the application of electric field. Interconnectivity between pores is clear enough to call this stage as intermediate stage of sintering. This interconnectivity gives the pores a cylindrical shape.

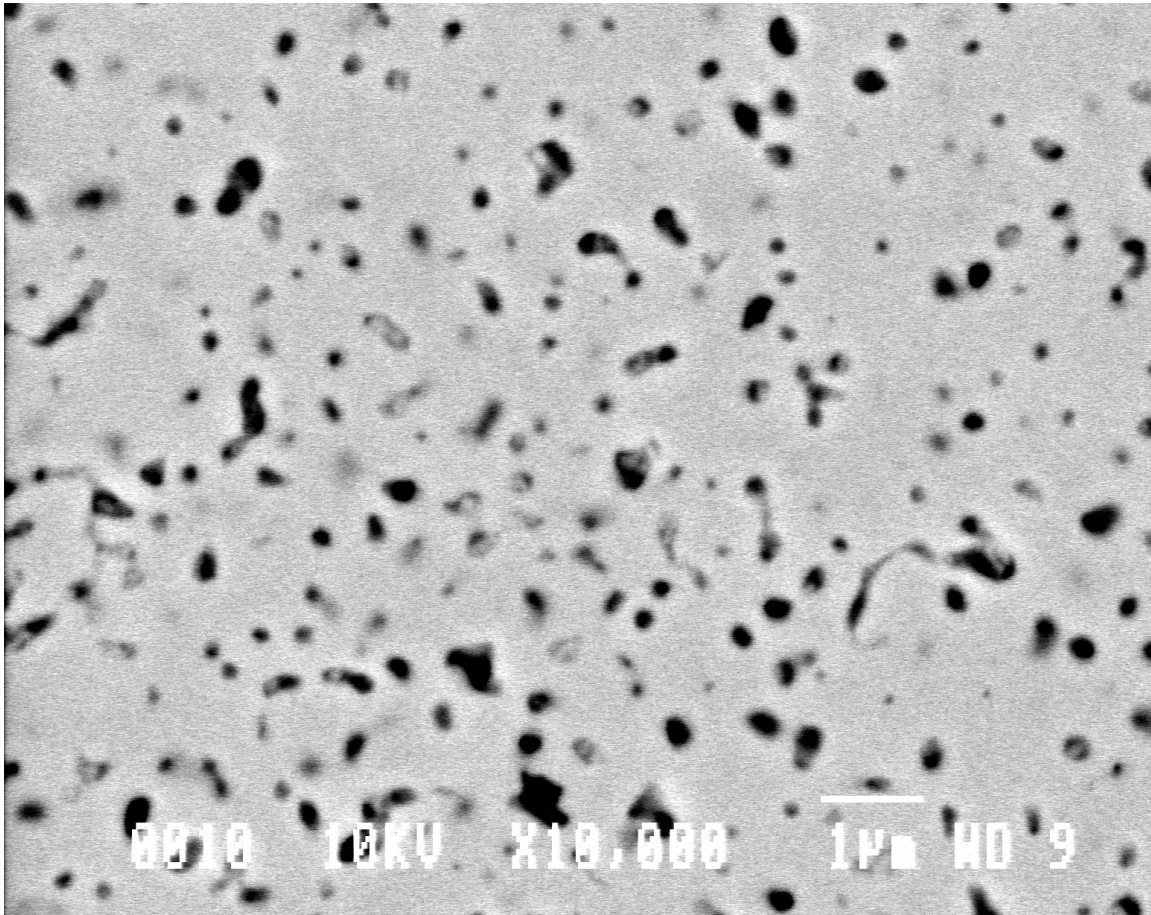


Figure 11c) Sintered at 1200°C with the application of electric field. Most of the interconnectivity between the pores is gone but pores are still coarse.

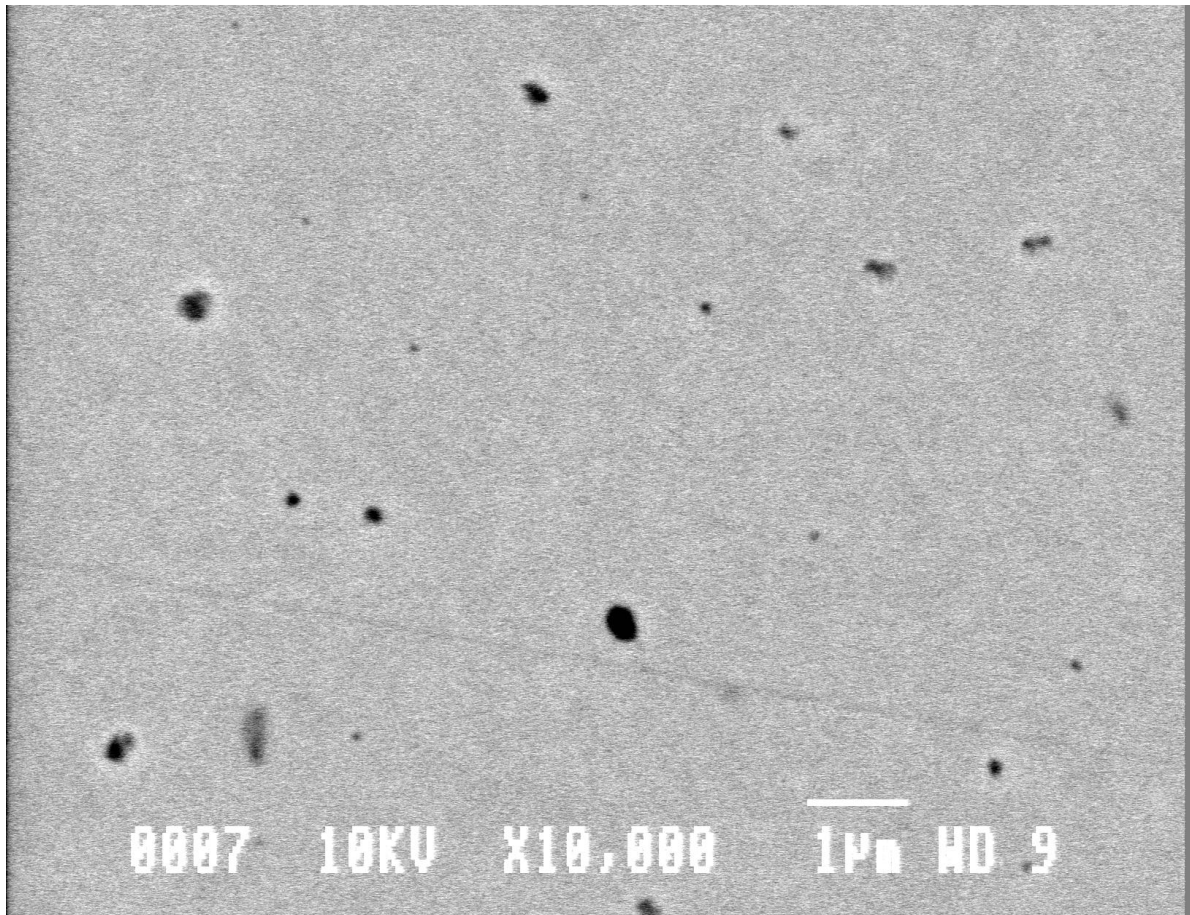


Figure 11d) Sintered at 1500°C by conventional sintering. Density value corresponds to 100% of relative density. Interconnectivity between the pores is completely disappeared giving solitary spherical pores.

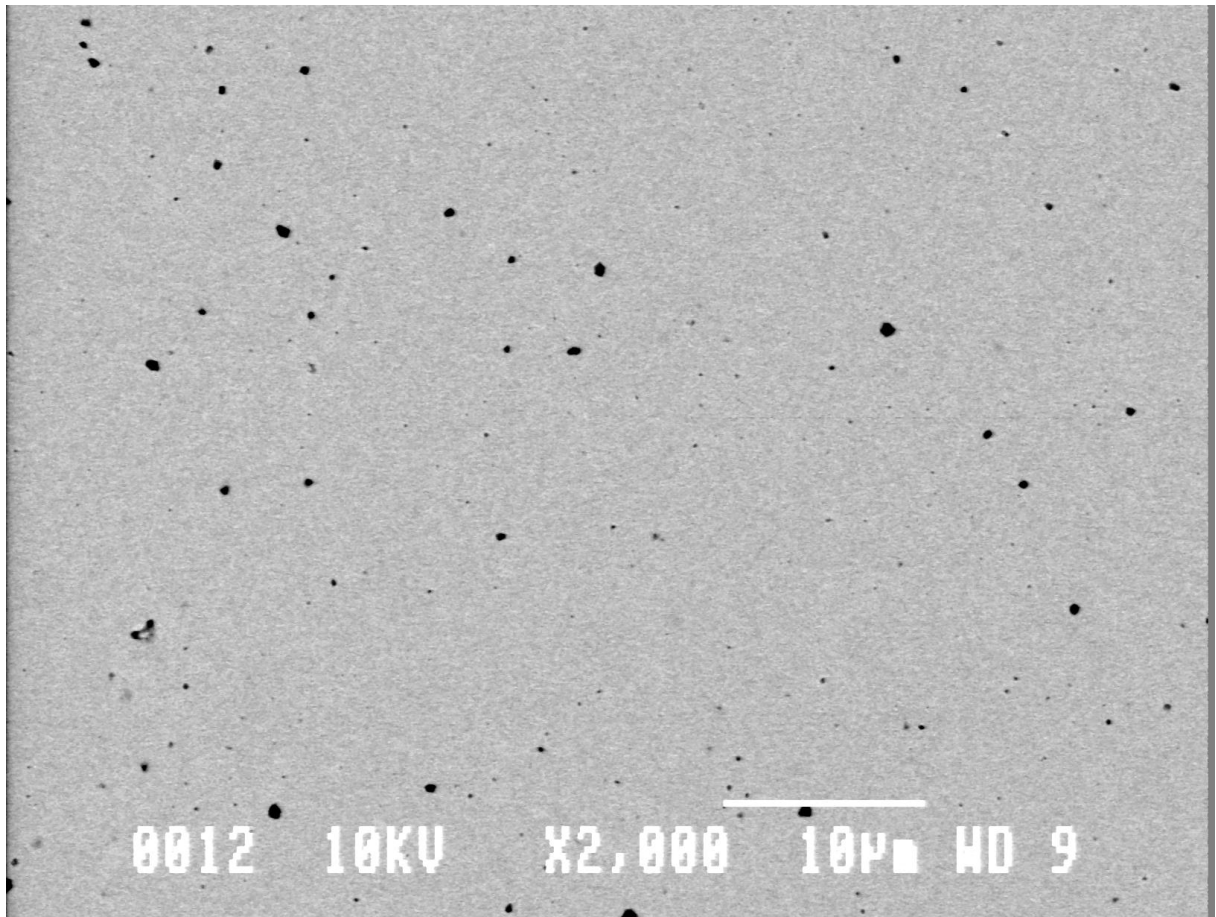


Figure 11e) Sintered at 1500°C with the application of electric field, fully sintered sample.

Figure 11(a,b,c,d,e): Micrographs of Y_2O_3 - ZrO_2 for both scenarios at different temperatures. Intermediate stage is readily affected by the electric current.

When sintering was performed at higher temperatures, there was no significant effect from the electric current as shown in the *micrograph e* in *Figure 11*. The reason might be that all the energy needed for an effective diffusion to occur is available when the temperature is sufficiently high, which results in that the addition of current does not play any major role at high temperature as discussed later in this section.

According to German shrinkage during the initial stage is given by: [10]

$$\left(\Delta L/L_o\right)^{n/2} = Bt / (2^n D^m) \quad (3.1)$$

Where $n/2$ is typically between 2.5 and 3, D is the particle diameter, t is the isothermal time and parameter m value depends on the mechanism of mass diffusion, generally it is taken as 3 for volume diffusion and 4 for surface diffusion. The parameter B is exponentially dependant on temperature and is defined as,

$$B = B_o \exp\left(-Q/RT\right) \quad (3.2)$$

Where R is the gas constant, T is the absolute temperature, and B_o is a collection of material parameters like, surface energy, atomic size, atomic vibration frequency and system geometry. Q is the activation energy. It is clear from equation (3.1) that shrinkage is inversely proportional to the grain size during the initial stage [10]

Randall also explained the densification during the intermediate stage, which follow as;

$$\rho_s = \rho_i + B_i \ln(t/t_i) \quad (3.3)$$

Where, ρ_s is the sintered density, ρ_i is the density at the beginning of the intermediate stage, B_i follows the equation (3.2), varies inversely with the cube of the grain size, thus have a substantial effect on densification. t_i is the time when intermediate stage starts, and t is the isothermal sintering time. [10]

Equation (3.2) and equation (3.3) explicitly describe the influence of grain size on densification, which are inversely proportional to each other. Hence, retardation in grain growth enhances densification. This is one of the reasons for the improved densification in the case of field assisted sintering as the electric field retards grain growth [2]. This phenomenon can be seen in the micrographs, *Figure 12*; and more clearly for CeO_2 - ZrO_2 case (shown later)

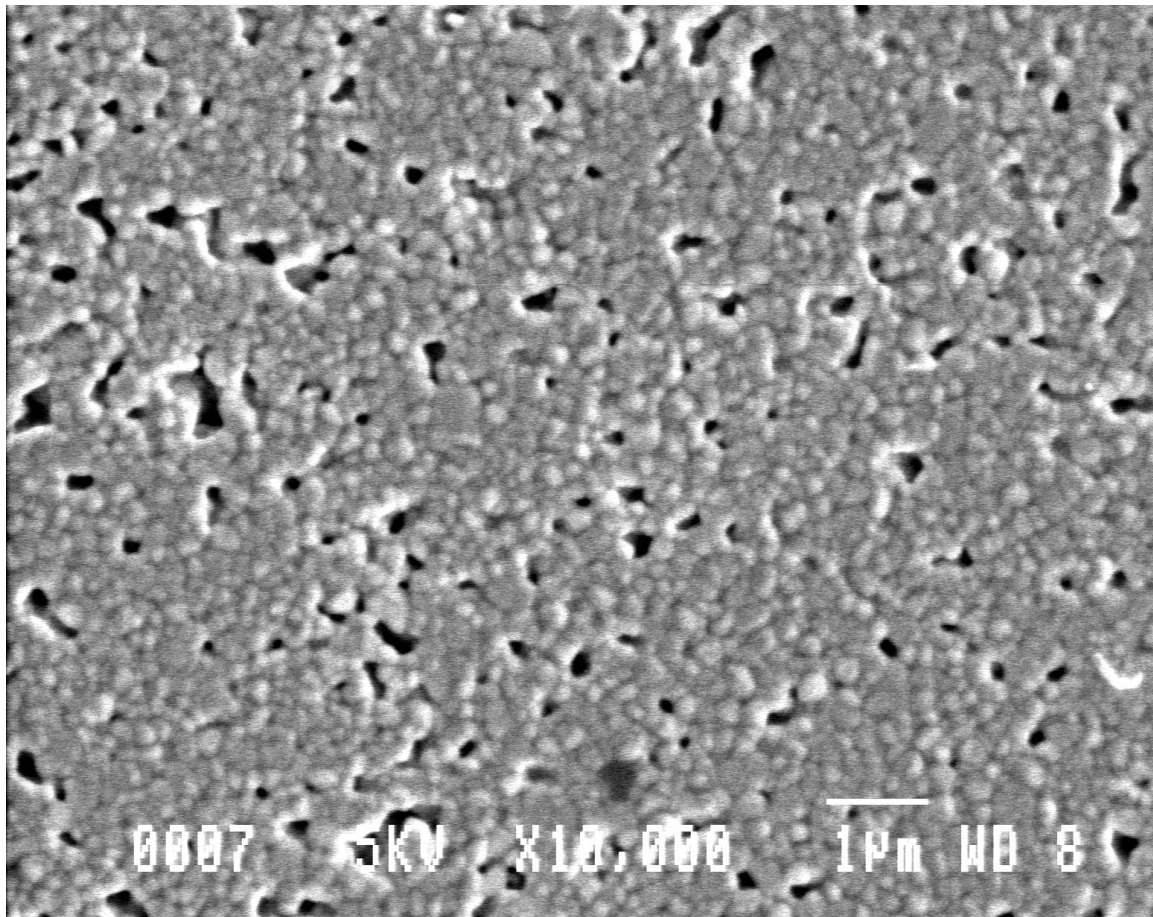


Figure 12a) $\text{Y}_2\text{O}_3\text{-ZrO}_2$ sintered (without field) at 1300°C.

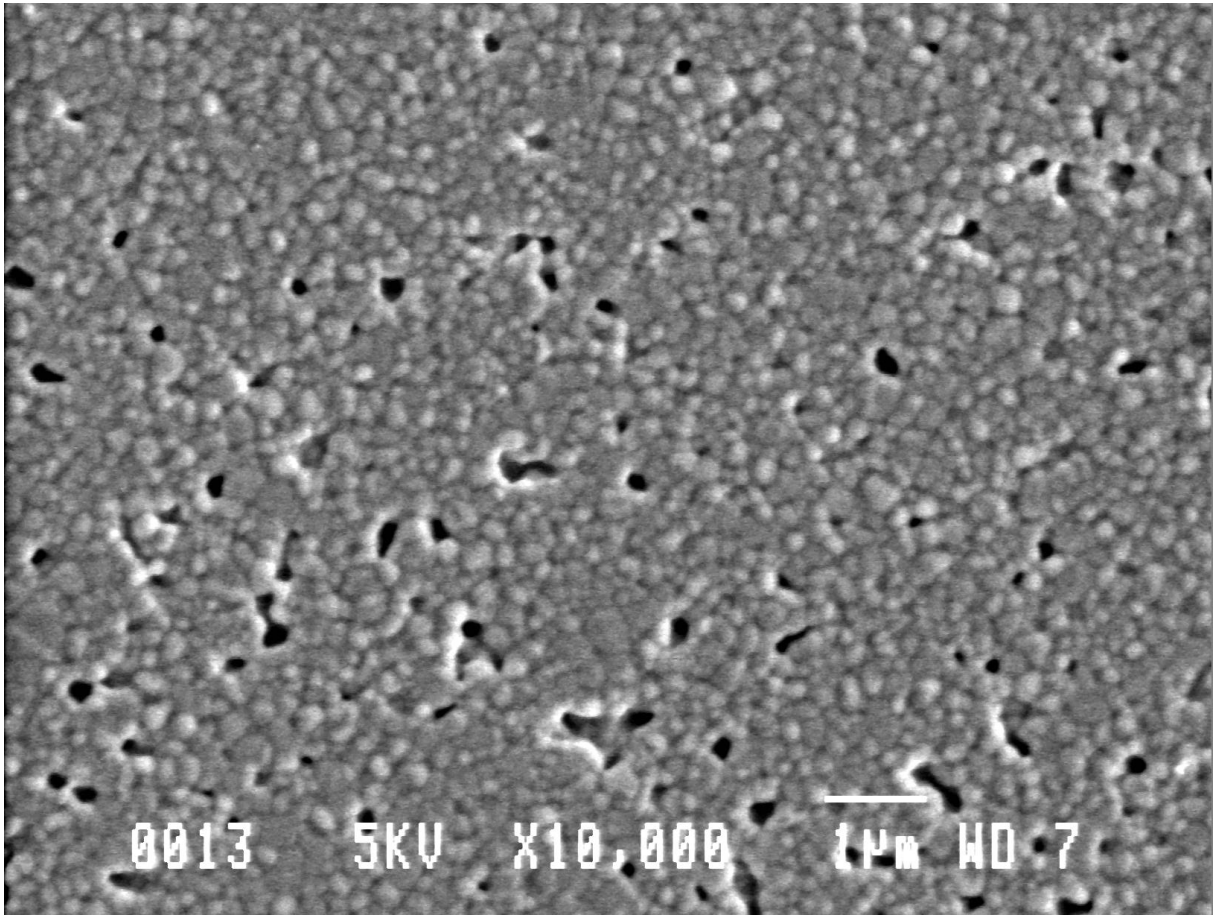


Figure 12b) Y_2O_3 - ZrO_2 sintered (with field) at 1300°C

Figure 12(a,b): Effect of electric current on grain growth. In conventional sintering process the microstructure is very uneven, though most of the grains are not coarse but still there are many large grains encapsulated by the small grains. In field assisted sintering, the microstructure is built on mostly small grains.

There exist a couple of suggestions on how the electric field retards the grain growth. According to Rishi raj et al; (i) “the electric field disturbs the space-charge defect chemistry, which has an influence on interfacial kinetics by changing either the preexponential, or the activation energy, or both, in the diffusion coefficient, or by altering the segregation of charged defects to the interface”. The second hypothesis is; (ii) the grain boundaries provide more resistance to current flow, thus producing the ‘Joule heating effect’. [2,6]

The first assumption is based on ‘space-charge model’. As described by the equation (1.4) each substitution of Zr with Y produces Y'_{Zr} ions. The pairs $(Y'_{Zr}-\ddot{V}_O)^\circ$ are formed due to the attractive interaction between opposite charges, and this leaves Y'_{Zr} ions

distributed in the lattice [19,26]. According to the space-charge model, if the solute (Y) with an effective negative charge is present in the bulk of the grain, then the surface in equilibrium must possess a countercharge, which is positive in this case [19,26]. The dopant (Y) in turn tries to segregate to the region adjacent to the surface as a space charge by Coulomb attraction, so that the charge neutrality is maintained. This emphasizes the presence of a layer of Y_{Zr}' ions at grain boundaries. This layer is called as space charge layer. The aftermath of this layer is the extra drag to the boundary mobility, resulting in the retardation of the grain growth [19,26].

It is thought that external field somehow alters the configuration of the space-charge layer [2].but it is very difficult to prove how it affects the space-charge layer and potentially no theory has been presented about this effect.

The second hypothesis is more prominent than the first one. It is assumed that grain boundaries acquire higher electrical resistance due to the space-charge layer. This higher electrical resistance gives higher temperature within the vicinity of grain boundaries because of the Joule Heating Effect [2,7].

The interfacial energy for the boundary migration is given as;

$$\gamma_w = \Delta H_w - T\Delta S_w \quad (3.4)$$

Where, γ_w is the interfacial energy, ΔH_w is the excess enthalpy and ΔS_w is the excess entropy of the grain boundary [2,7]. It is clear from the equation (3.4) that increase in temperature will lead to the minimum in interfacial energy at grain boundary as explained in the *Figure 13*:

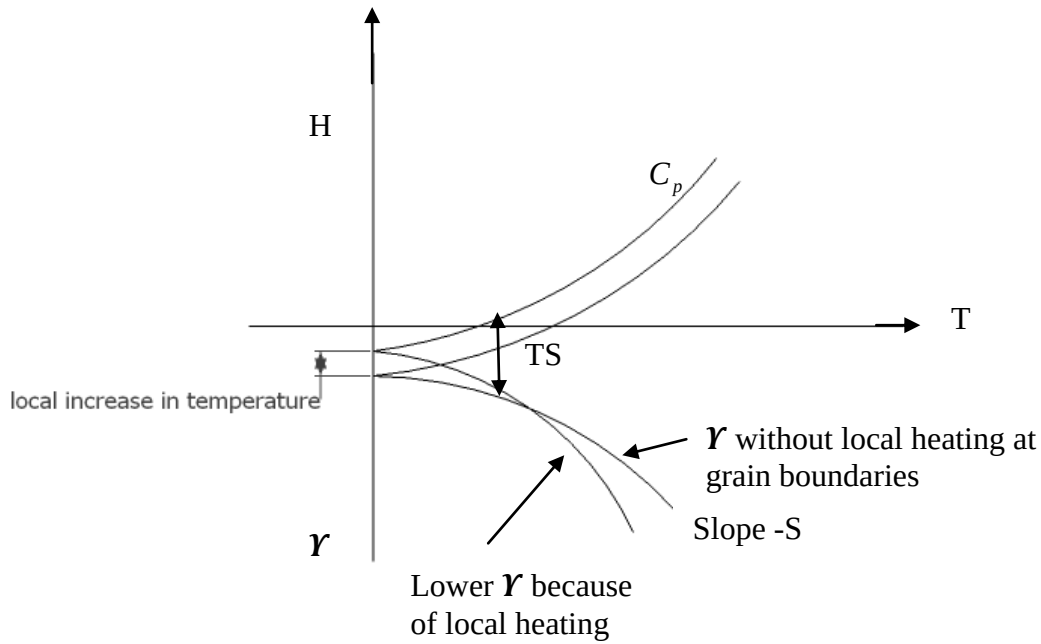


Figure 13: Effect of higher temperature at grain boundaries. It was assumed that grain boundary is a system having unit area. Local heating will reduce the interfacial free energy adding a kinetic barrier to boundary movement.

This local minimum at grain boundary will reduce the driving force for the boundary movement, adding a kinetic barrier to the motion of the boundary, thus effectively pinning it.

Apart from decreasing the driving force for boundary migration, local joule heating also increases the grain boundary diffusion, eventually increasing the densification rate. Although joule heating increases the diffusion along grain boundaries and across grain boundaries but still it is believed it retards the grain growth, as by equation (3.5) grain growth is [15];

$$\tilde{D}^2 = D_0^2 + Kt \quad (3.5)$$

Where, $\tilde{D}$ is the grain growth rate, $K = 4\alpha M\gamma$, t is the time, D_0 is the initial size of grain at $t=0$

It is clear that $\tilde{D}$ depends on K , which itself depends on boundary mobility M and interfacial energy γ . So if, γ is reduced and M is increased then the product of the two still can be lower. It should also be noted that mobility itself depends on the interface kinetics [15].

There could be another reason for this retardation in grain growth during the intermediate stage when a higher driving force is present to reduce the surface energy. When a current is applied through the sample, the bulk diffusion is increased. This allows the surface energy to be reduced at a lower temperature and in a shorter period of time, which increases the densification rate during the intermediate stage and gives less time for the grains to grow.

The increase in the internal temperature due to the Joule Heating Effect is shown in the *Figure 14*:

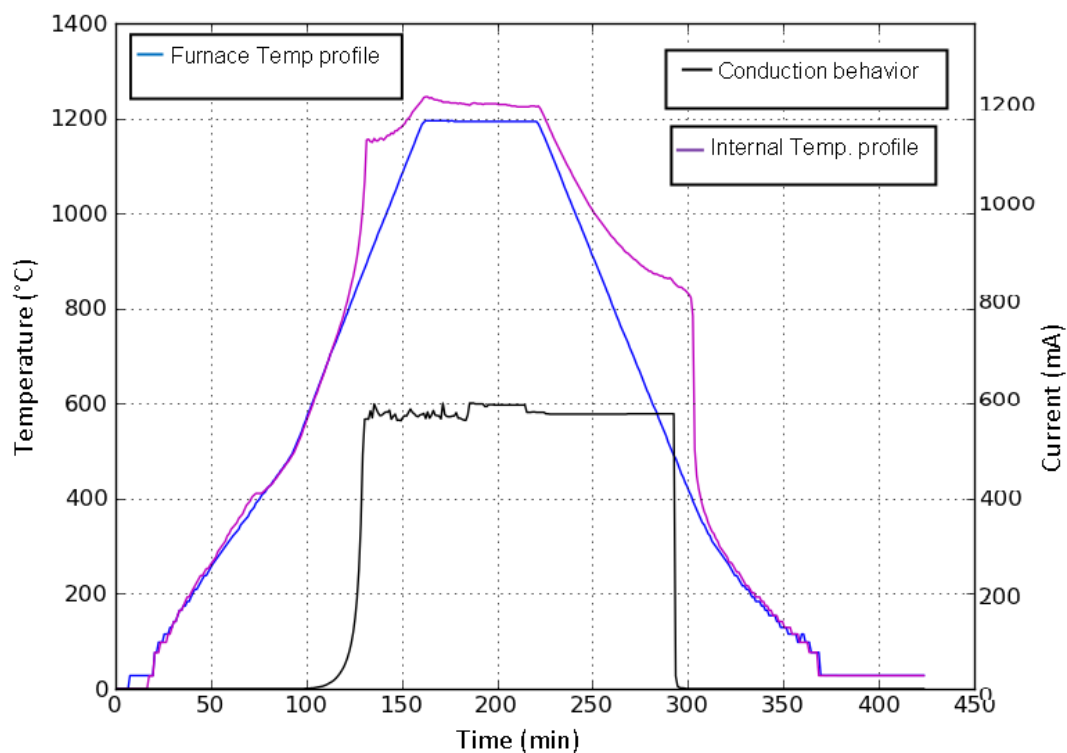


Figure 14: Joule heating effect at 1200 °C, 30V and current of 600mA.

It is clear from the *Figure 14* that as conduction increases the internal temperature of the sample increases and when it reaches to its full conduction, the internal temperature abruptly increases but then this increase gradually lessens and almost remains constant with the current during the holding period. The reason for this behavior is at low temperatures the resistance of the sample is very high due to open porosity but as temperature and current increases sample starts to densify lowering the resistance gradually resulting in decrease in the internal temperature with time.

The influence on the internal temperature due to joule heating was more prominent at lower temperatures and was also depending on the current, *Figure 15*.

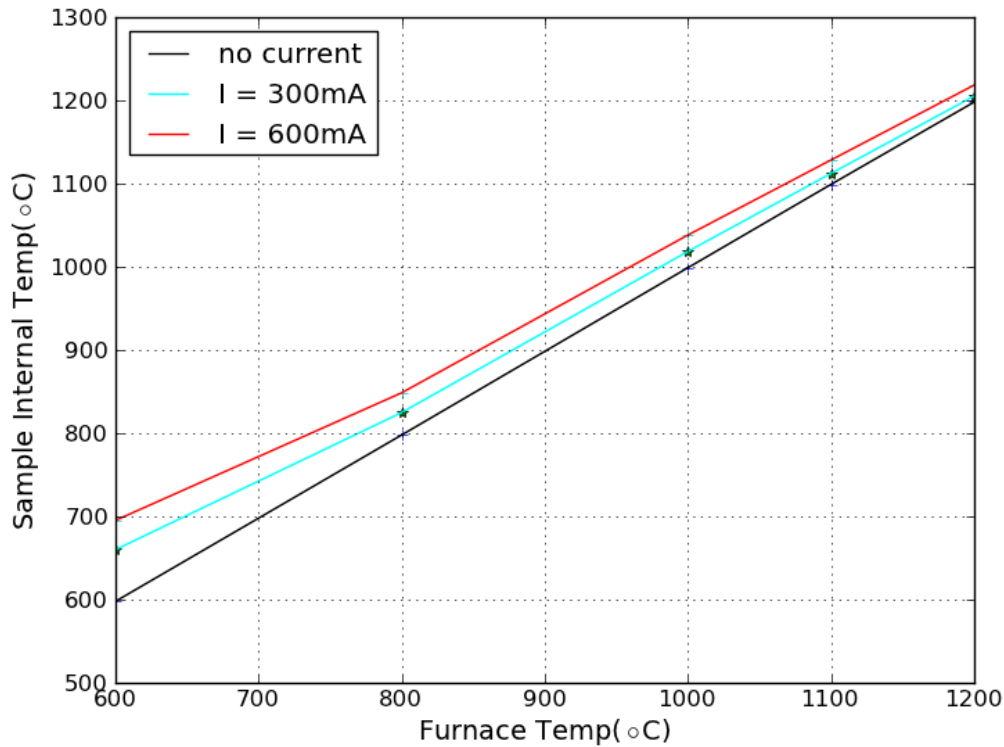


Figure 15: Joule heating effect at different temperatures.

The reason for the temperature dependence on the joule heating could be that the electric resistance of the grain boundaries increased as the temperature was decreased. This higher electric resistance at lower temperatures would thus give an increased heating of grain boundaries.

To evaluate the influence from the joule heating on densification, the densities of the field assisted sintered samples and conventionally sintered samples, in *Figure 9* were in addition to the furnace temperature, also plotted as a function of the sample temperature (*Figure 16*). When the sample temperatures were considered instead of the furnace temperature, the difference in density between the materials sintered with and without an electric field was then slightly reduced. There were, however, still a significant increase in density when an electric field was used, which indicates that the increased densification was not mainly due to joule heating. The current has thus a large influence on other factors such as increased ion's movement and electric field effect on space-charge layer to improve densification.

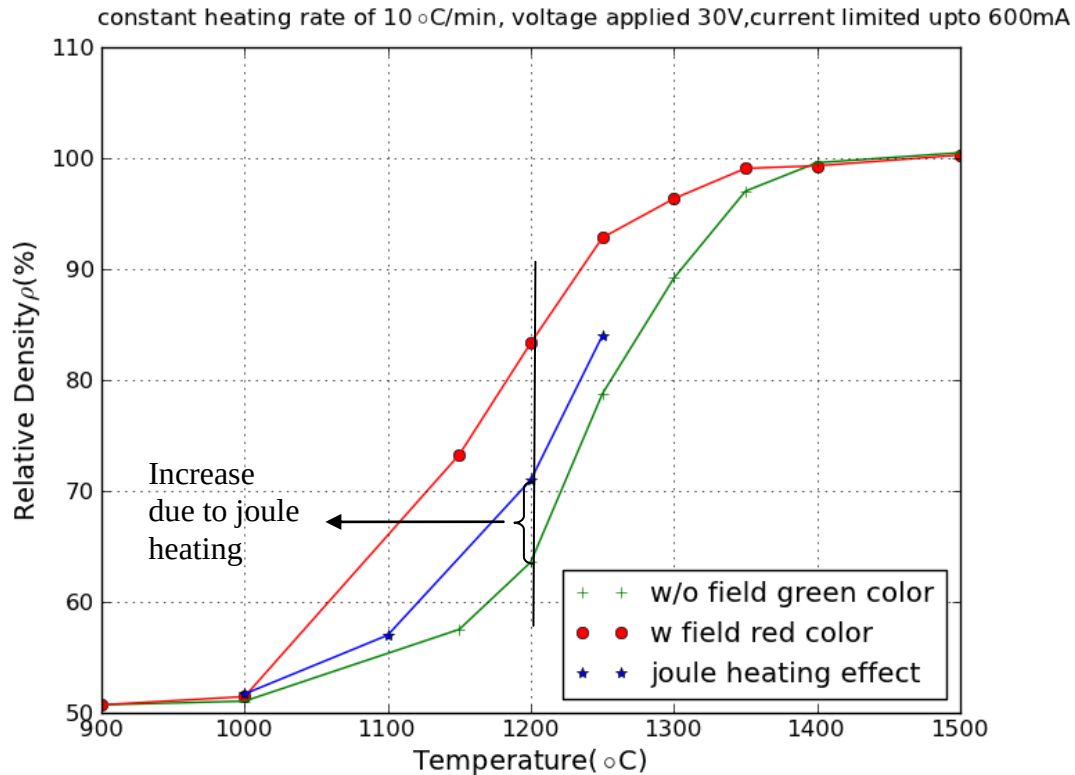


Figure 16: Shows the difference in internal temperature and sintering temperature at different relative densities in field assisted sintering. The blue line is the sample internal temperature line. Approximately 30-40% increase in density is due to joule heating in field assisted sintering.

3.2 Voltage effect

The effect of voltage on the densification of field assisted sintering is shown in Figure 17 and shows that the density increases with increasing voltage up to 30V. At voltages above 30V, the central and the outer part of the sample was densified differently resulting in an uneven densification and reduced density. This was because of the onset of flash sintering above 40V/cm with the most densified area in the centre [7], Figure 18.

At 1200 C, constant heating rate of 10C/min, current limited upto 600mA, holding time 1hr

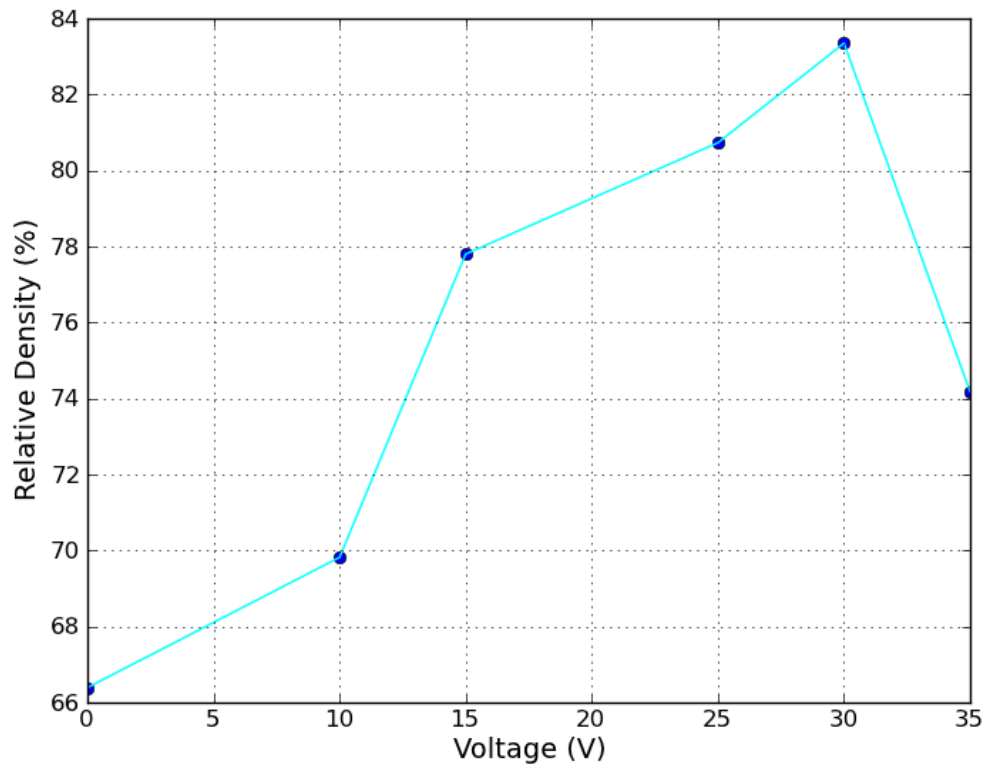


Figure 17: Density of sintered materials for various voltages.

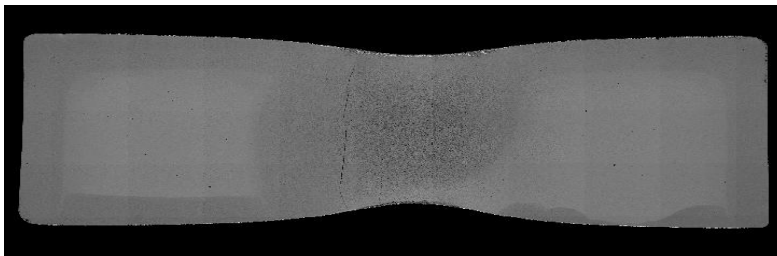


Figure 18: Density variations within the sample when voltage above 30V was applied

The applied voltage determined the required temperature at which the conduction was initiated and will thus also influence the contribution from the current on the densification (Figure 19). When the temperature was reduced, the conduction ended at around 700°C when 30V was applied while for higher voltages the conduction remained even at room temperature due to the internal joule heating of the sample.

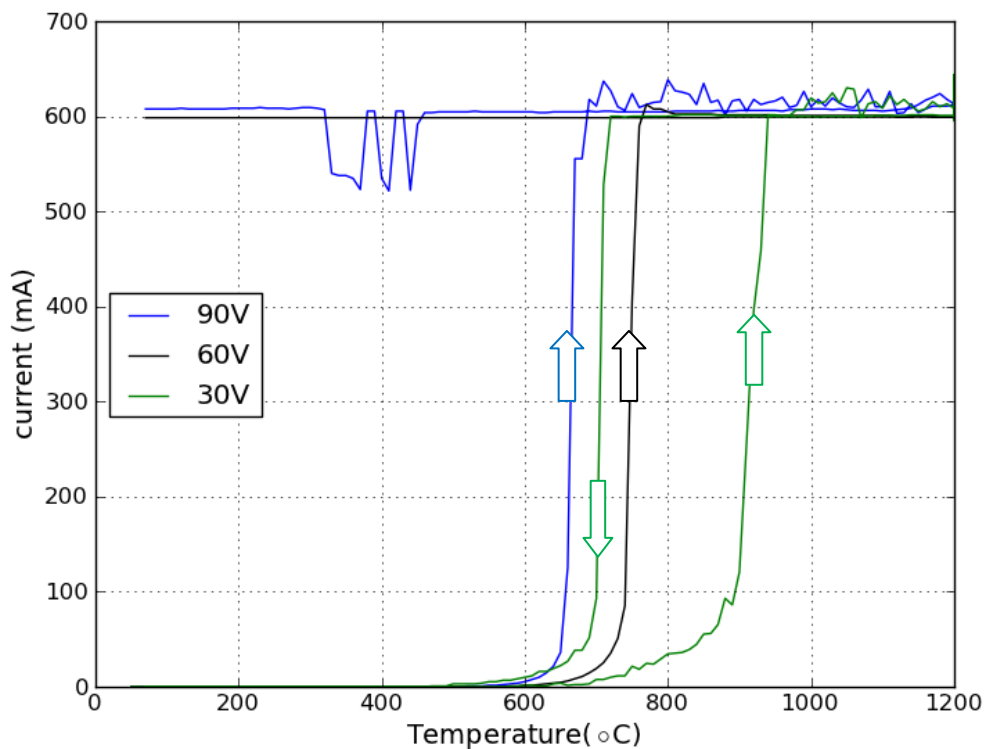


Figure 19: Voltage reliance of the Y_2O_3 - ZrO_2 (max. temperature $1200^{\circ}C$ and current of 600mA). The aftermath of increased voltage value is early conduction. The total time to achieve the maximum conduction is also reduced. 90V and 60V samples were conducting until the end. This is because of the extensive internal heating at lower temperatures due to the conduction as discussed above. This internally high temperature maintains the conduction.

3.3 Effects of Current Density

It was found during the experiments that current density is more important than the electric field strength. Densification primly depends on current density.

At 1200 C, constant heating rate of 10C/min, current limited upto 600mA, holding time 1hr

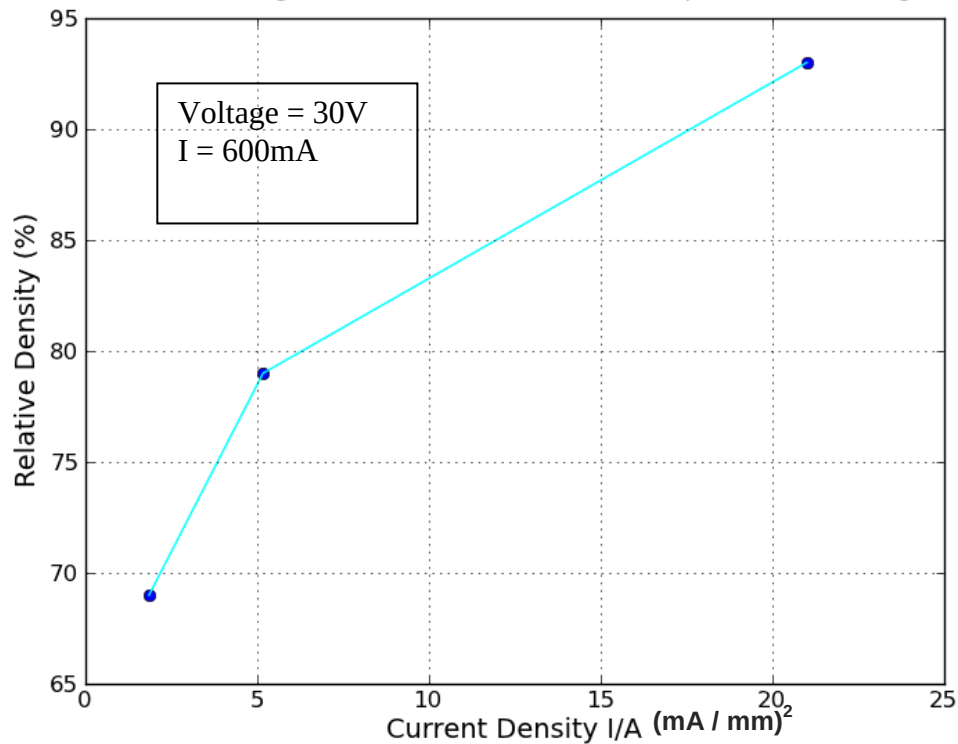


Figure 20: Current density versus the temperature for 3 different diameters 6mm, 12mm and 20mm samples. The current was same for all of the three samples, i.e. 600mA.

It is clear from the Figure 20 that with increasing current density relative density increases irrespective of the voltage applied.

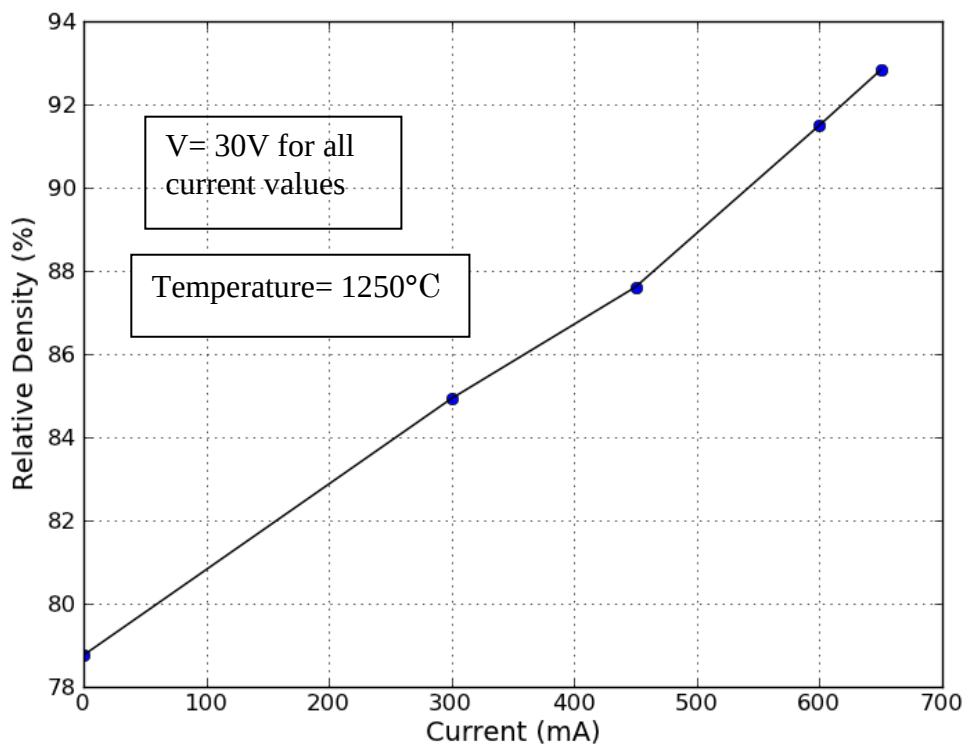


Figure 21: Relationship between the current and relative density is almost linear with increasing trend. It should be kept in mind that very high current intensity may lead to cracking and uneven density distribution.

On the other hand, electric field/voltage does not play any major role other than affecting space-charge distribution which is still not fully understood. Its contribution is the same as of voltage that is it governs the conduction behavior.

3.4 Time Effect on Sintering Rate

At the same temperature, voltage, current and heating rate, the densification increased parabolically with the holding time for both sintering procedures (*Figure 22*).

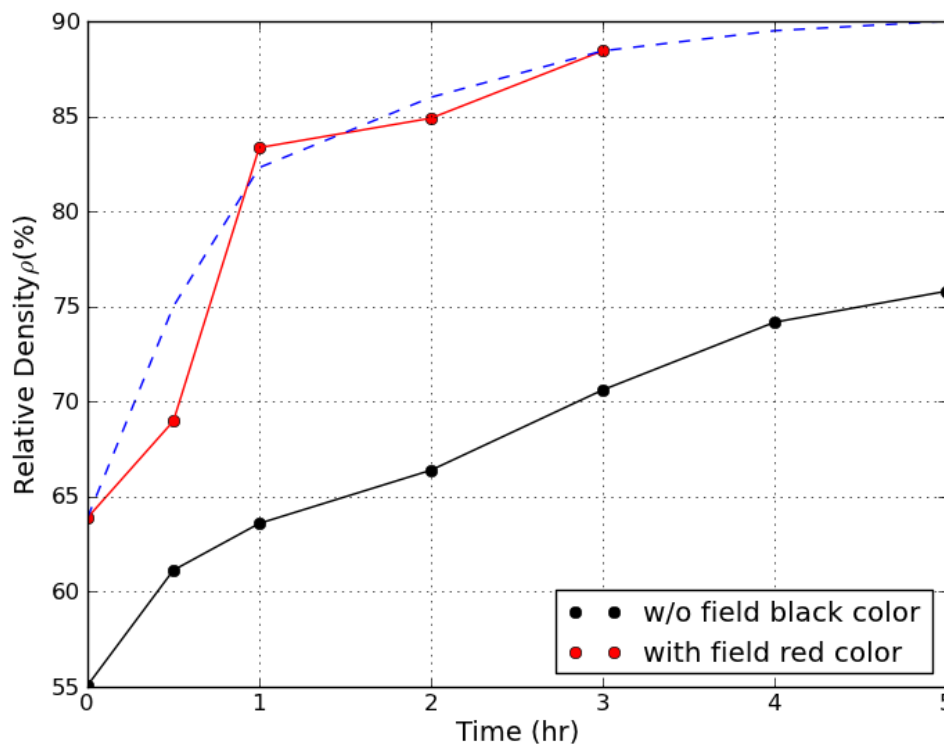


Figure 22: Parabolic relationship between holding time and relative density for the same temperature, voltage, current and heating cycle conditions. The incomplete graph in the case of field assisted sintering is due to the samples fracturing at higher holding times.

3.5 Field assisted sintering of other metal oxides

3.5.1 Ceria-Stabilized Zirconia ($\text{CeO}_2\text{-ZrO}_2$)

The density of ceria stabilized zirconia sintered with and without an electric field is shown in Figure 23.

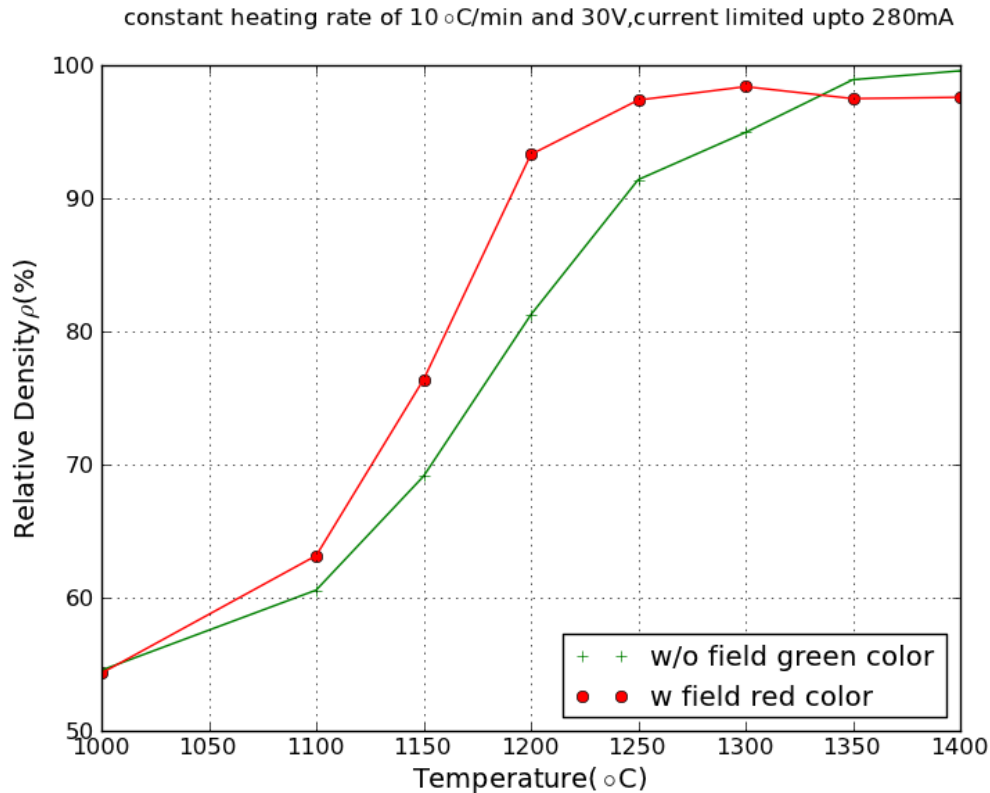


Figure 23: Comparison between two sintering rates for $\text{CeO}_2\text{-ZrO}_2$. Full densification was achieved at 1400°C by sintering for 1 hr. The low density at the higher temperatures in field assisted sintering was because of cracks (the experimental procedure and cycles rates were similar as for the $\text{Y}_2\text{O}_3\text{-ZrO}_2$ case)

The conduction behavior of $\text{CeO}_2\text{-ZrO}_2$ is quite different from the $\text{Y}_2\text{O}_3\text{-ZrO}_2$ one, as cerium also has 4+ valence like zirconium, so its addition does not create any oxygen vacancies [24]. Yet, it showed significant conductivity below 1200°C and at higher temperatures, the current was limited by the power supply like the $\text{Y}_2\text{O}_3\text{-ZrO}_2$ sample, Figure 24.

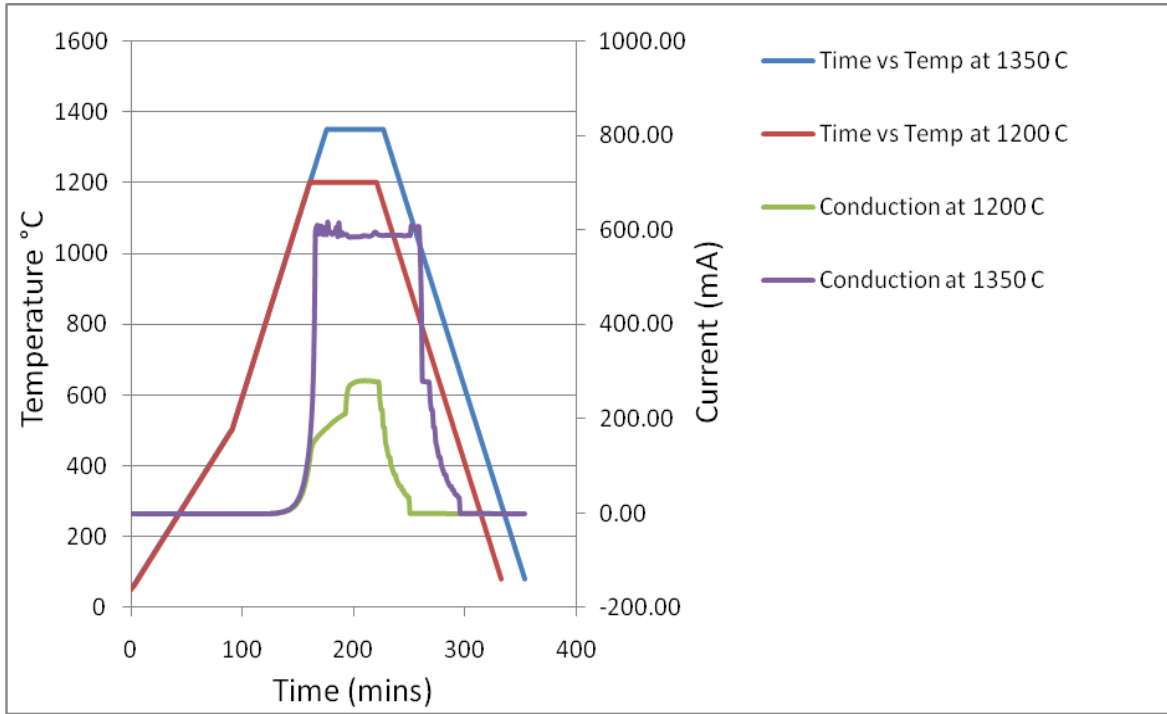
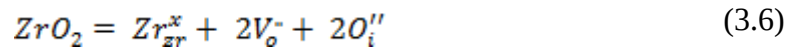


Figure 24: Conduction behavior of $\text{CeO}_2\text{-ZrO}_2$ for two sintering cycles with top temperatures of 1200°C and 1350°C . In both cases, the conduction was initiated at a very minuscule level around 850°C and reached to the maximum conduction of 280mA in the case of 1200°C (the green line) while for 1350°C it reached to the limiting value of 600mA (the mauve line).

It was proposed by R.F. Reidy et al. that Ce stabilized Zr conduction depends on oxygen partial pressure, ceria content percentage and temperature [24]. According to the authors, there are two conduction behaviors for 12 mole % of ceria content; one is temperature dependent and the other is both oxygen partial pressure and temperature dependent behavior. As these experiments were performed in the furnace working at the moderate oxygen partial pressures ($1 > P_{\text{O}_2} > 10^{-9} - 10^{-15} \text{ atm}$) it was assumed that at 1200°C , the oxygen partial pressure would not influence the results significantly and the conduction behaviors would mainly depend on the temperature dependent domain (shown in Figure 25) which follows the anti-Frenkel defect behavior [24]



Where, $V_{\text{O}}^{\bullet}$ is oxygen vacancy and $O_{\text{i}}^{\bullet\bullet}$ is oxygen interstitial defect.

As cerium ions have the same valency (+4) as zirconium, it does not create any additional oxygen vacancies. Hence, it was assumed that at moderate oxygen partial pressures and temperatures below or equal to 1200°C the conduction is solely

dependent on the inherent oxygen vacancy defects [24]. That could be the reason of limited conduction below 1200°C.

There are a couple of reasons for the peculiar behavior of enhanced conduction above 1200°C, but the most common one is the n-type semiconductor behavior. Referring to the *Figure 25* again, the threshold oxygen partial pressure value, which separates the oxygen dependent and oxygen independent conductivity regions increases as temperature increases, and it may happen that at a certain temperature it became equal to moderate oxygen partial pressure, giving conduction because of both regions at that particular temperature. This may be the reason of high conduction at temperatures above 1200°C.

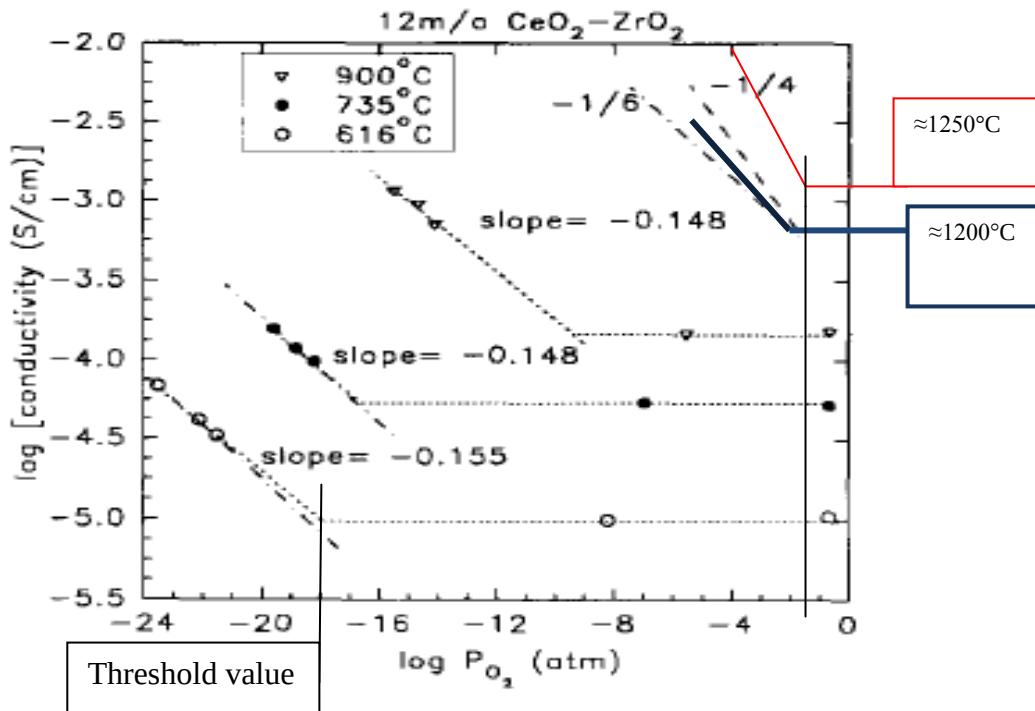
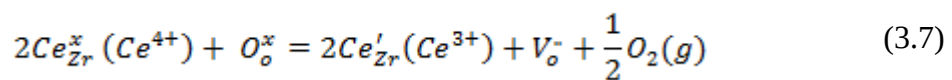
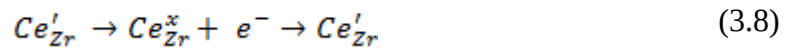


Figure 25: Temperature dependence of threshold oxygen partial pressure.[27]

According to R.F. Reidy et al. the slope of oxygen dependent domain suggests the n type semi conductive behavior is present which is due to the reduction of cerium ion; according to Casselton [25],



These reduced cerium ions generates electrons, which then conduct through hopping in-between the cerium ions by reaction;



The blackening of CeO₂-ZrO₂ samples sintered at temperatures above 1200°C is indications of the presence of a reduction of cerium ions, see *Figure 26*.



Figure 26: Blackening of a CeO₂-ZrO₂ sample.

The electric field increases the densification of CeO₂-ZrO₂ in a similar way as for Y₂O₃-ZrO₂ by retarding the grain growth and increasing diffusion due to effective joule heating at grain boundaries. The reduction of the grain growth for materials sintered at 1300°C is clearly visible in the SEM images, *Figure 27*.

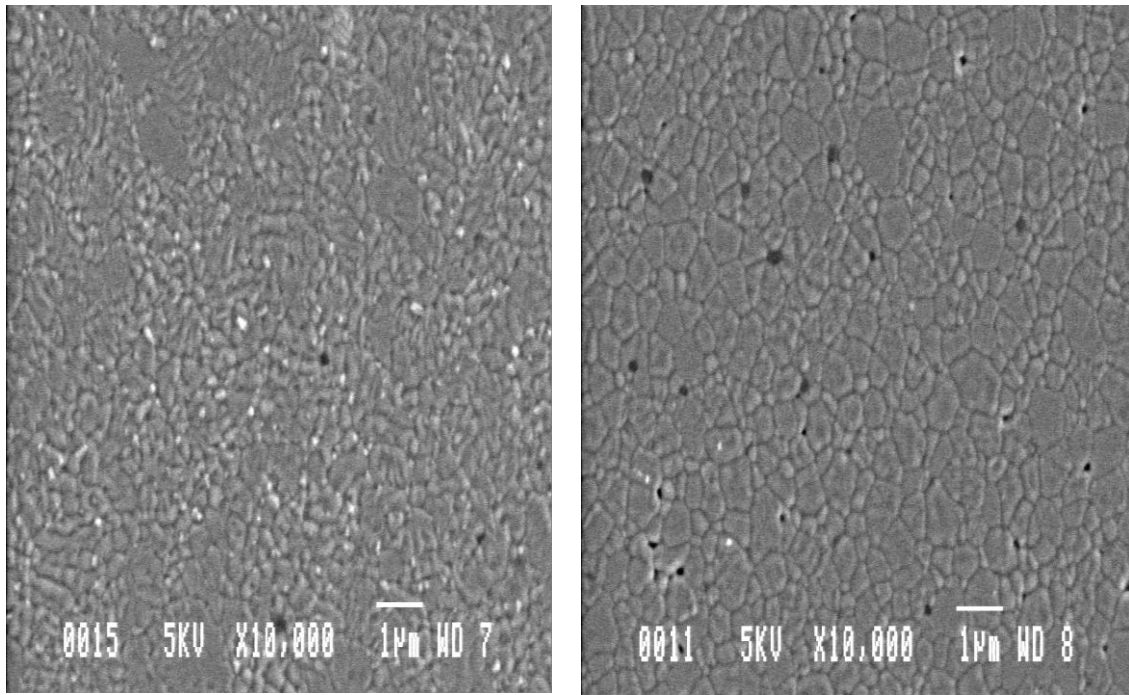


Figure 27: Microstructure of CeO₂-ZrO₂ sintered at 1300°C with (left) and without field (right). The use of an electric field shows that the grain size can be significantly reduced.

3.5.2 Mechanical Testing of CeO₂-ZrO₂

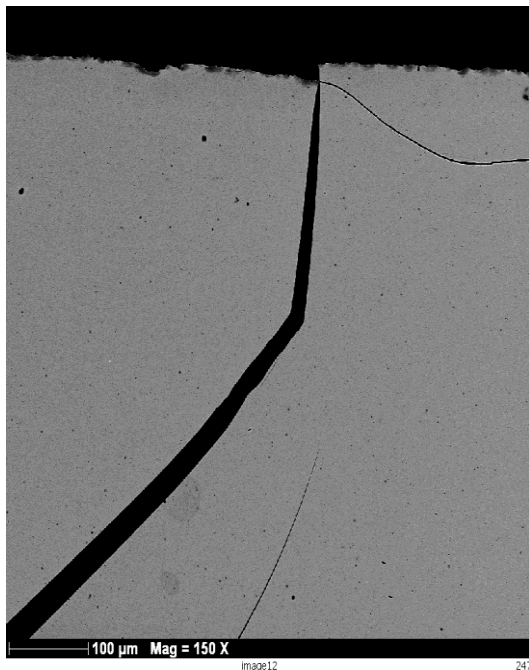
The average strength value for conventional sintering was 623 MPa and 602 MPa for field assisted sintering. With the spread in strength taken into account the biaxial flexural testing result showed that there is no increase in the strength of CeO₂-ZrO₂ in spite of the smaller grain size in case of field assisted sintering. One possible reason for this could be due to a few larger grains present in the material, which diminished the beneficiary effect of smaller grains (see *Figure 27*). Referring to *Figure 27* some big grains are clearly visible. This may increase the average grain size. The low strength may also be due to stresses which occurred due to uneven densification in case of field assisted sintering.

Other possible reason for low strength in case of field assisted sintering could be that the transformation toughening also depends on grain size. Transformation toughening mechanism is more prominent for big grains as the transformed volume increases the strength increases.

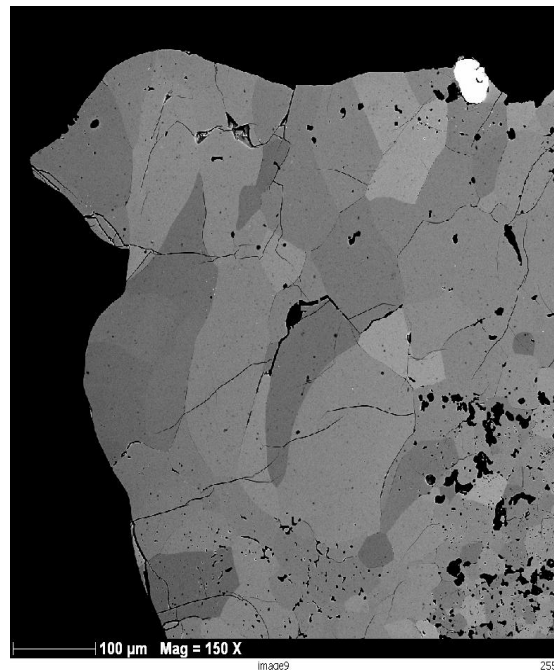
The narrow distribution between the values in case of field assisted sintering shows that same type of defect is present.

3.5.3 Titanium Oxide (TiO₂)

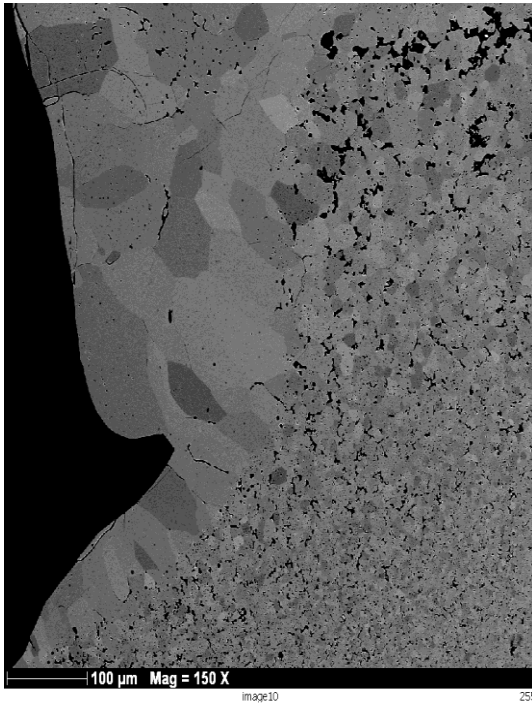
In the case of TiO₂ no such increased densification behavior was noted upon application of electric field. The reason for this lies in the chemistry of titania. Pure titania is not an ionic ceramic. It does not have oxygen vacancy defects to conduct electricity by bulk diffusion as in yttria and ceria doped zirconia. The only way of conduction is through electronic conduction, which was not found to be initiated until a temperature of 850°C was reached. However the conduction was not found to influence the densification of the titania material studied. When sintered at 850°C, the fine grained titania powder used reached a density of around 95-98% and an almost fully dense material was reached at 875°C and the current would thus not be able to significantly influence the densification. However it affects the microstructure, see *Figures 28 and 29*.



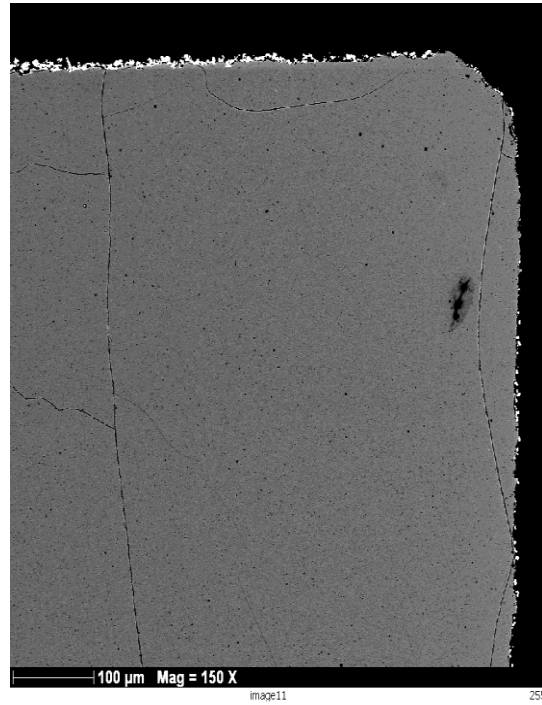
a) Center, without field.



b) center, 60V



c) Away from center, 60V



d) end corner, 60V

Figure 28: Microstructure analysis of TiO_2 sintered at 850°C .

Figure 28(b) shows that current has a huge effect on TiO_2 microstructure. Instead of retarding grain growth it has increased the grain growth (this effect is further discussed in next section). This effect is more prominent at the center. As the distance from center is increased this effect vanishes, *Figure 28(c, d)*.

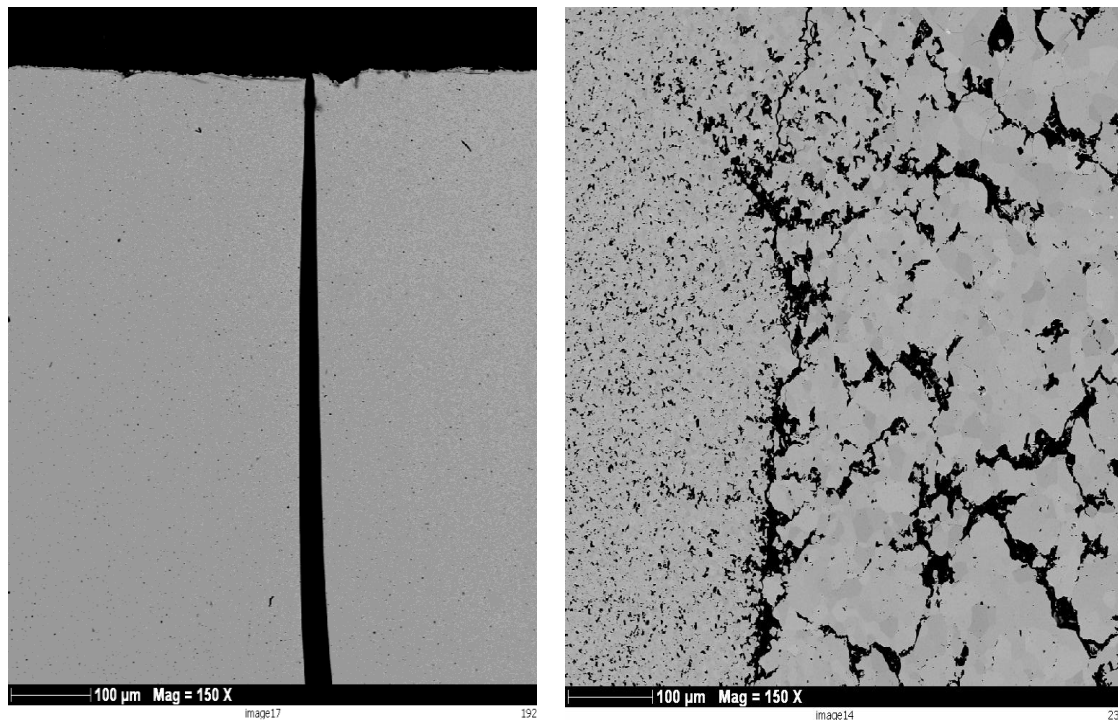


Figure 29: TiO_2 densified at 1000°C . Left conventional sintering microstructure. Right figure shows microstructure for field assisted sintering, voltage was 60V.

3.6 Effect of Current at Higher Temperatures

There could be another reason of grain growth retardation by the application of current. Current effectively increases the densification rate at the intermediate stage of sintering by productive local joule heating, producing increased grain boundary diffusion. The total time spent at the intermediate stage will thus be lower, giving less time for grains to grow. Hence, grain size will remain smaller at the end of intermediate stage.

However, at higher temperatures near the full densification temperature current effects on microstructure are totally different. If sufficient time is provided then excessive energy of the local joule heating results in a coarser microstructure, compared to the microstructure of conventional sintering sample, as shown in *Figure 30*:

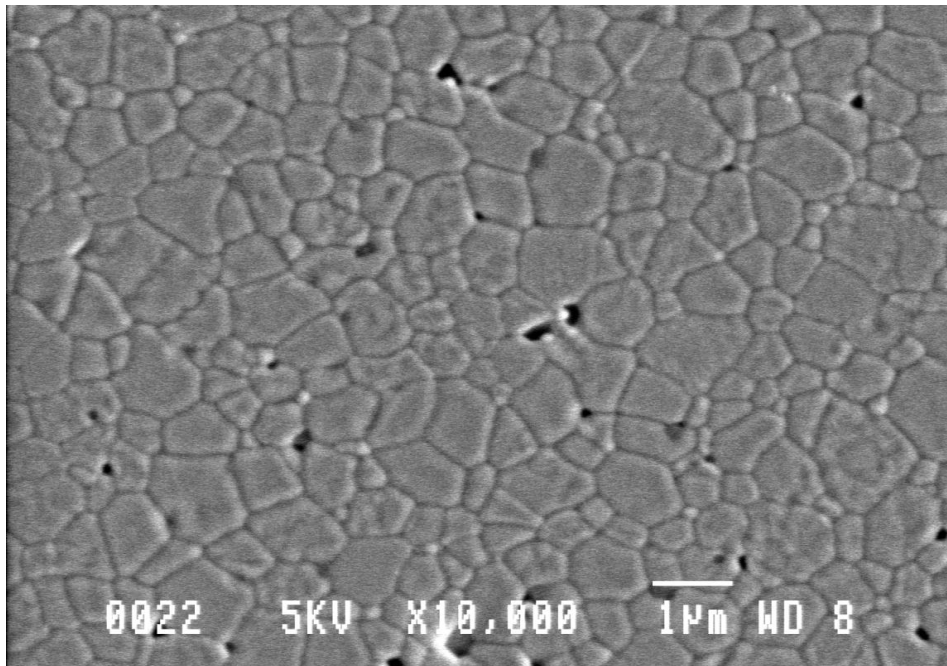


Figure 30 (Image 1): $\text{CeO}_2\text{-ZrO}_2$ at 1400°C without field assisted sintering

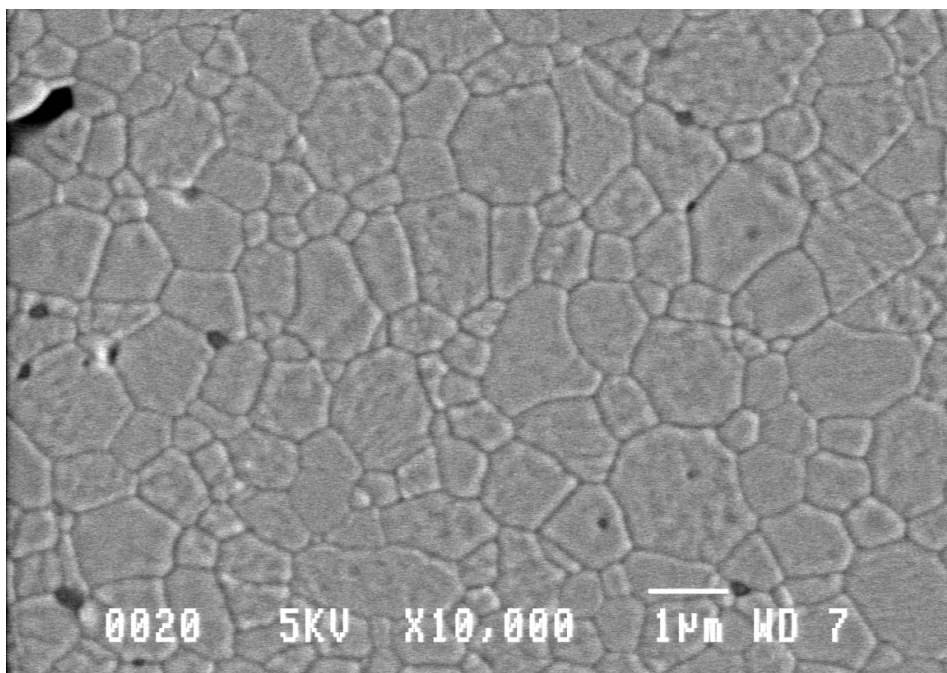


Figure 30 (Image 2): $\text{CeO}_2\text{-ZrO}_2$ at 1400°C with field assisted sintering

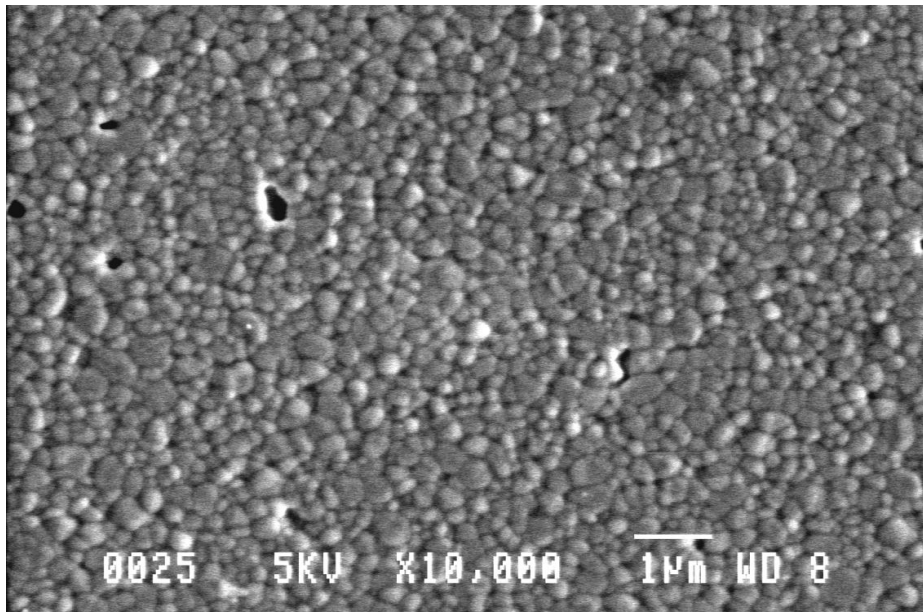


Figure 30 (Image 3): $Y_2O_3-ZrO_2$ at $1400^\circ C$ without field assisted sintering

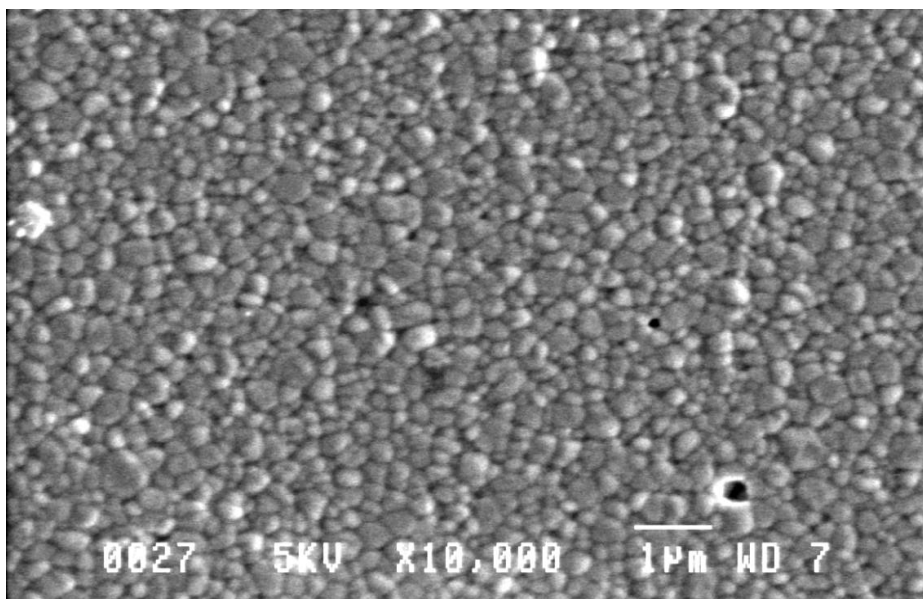


Figure 30 (Image 4): $Y_2O_3-ZrO_2$ at $1400^\circ C$ with field assisted sintering

Figure 30: Microstructures of CeO_2-ZrO_2 and $Y_2O_3-ZrO_2$ at $1400^\circ C$ for with and without field assisted sintering. There is a clear indication of large grain size in the case of CeO_2-ZrO_2 field sintering. This is because CeO_2-ZrO_2 is more susceptible to grain growth at higher temperatures if sufficient time is provided. For $Y_2O_3-ZrO_2$ there are more small grains (on average) in the case of without field sintering than with field sintering, giving the indication of grain growth.

3.7 Errors Estimation

The final density measurements used to evaluate the influence from the field assisted sintering may further depend on various errors in the experimental procedures performed such as fabrication of the green body, sintering and density measurements.

In the preparation of the green bodies, the variation would mainly be influenced by the compaction pressure, however the variation in pressure, which was assumed to be rather small. When an isostatic compaction pressure of 300MPa was used, a small variation of the pressure would however not contribute to a significant change in green density.

During densification, the real furnace temperature may deviate from programmed, but the difference would be the same for all sintering experiments when performed in the same furnace and would thus not influence the relation between the samples in the study. The current and the voltage were set for each sintering cycle. A variation of the voltage could be in the range of 0.2V and the current in the range of 10mA. With the often used voltage of 30V and 600mA, such a variation would influence the power by less than 2.5%.

The density measurements are normally done with accuracy around 0.1%, however, the error of the density measurements for the samples obtain by field assisted sintering might be somewhat higher due to cracks within the sample. Another reason for a variation of the density within or between samples sintered with a field, which does not need to be an error, can be due to an uneven densification caused by the transfer of current, internal sample temperature etc.

Strength in a brittle material is determined by the largest defect in tensile stress. This means that there is a distribution of strength values. The strength has been calculated as the mean of 6 strength measurements (individual values in appendix C).

Chapter Four

Conclusions and Future Work

4.1 Conclusions

The research presented in this thesis focused on the novel consolidation techniques FAST and FLASH by which sintering / densification rates have been enhanced considerably. Experiments were carried out on three different types of ceramic materials; two ionic, $\text{Y}_2\text{O}_3\text{-ZrO}_2$, $\text{CeO}_2\text{-ZrO}_2$ and one non ionic TiO_2 . It was found that electric current rather than electric field is the root cause of enhanced densification in such electrically controlled sintering techniques. Current intensity and density both are very important in controlling the densification behaviour. Electric field only governs the conduction behaviour, thus controlling the onset of the FLASH sintering. The reduction in grain growth found during these experiments suggested that the electric current halts the grain growth, indirectly enhancing densification rate. Two main factors controlling grain growth could be; Joule heating at grain boundaries and alteration of space-charge layer due to applied field. The first factor is more likely than the other. Joule heating at grain boundaries pins boundary's movement by effectively lowering the interfacial free energy, indirectly lowering the Gibbs free energy for grain growth.

In the case of non-ionic ceramic TiO_2 , however no such increase was found because of the non-conductive behavior before full densification temperature.

The mechanical testing of ceria stabilized zirconia samples showed that there is no increase in strength of the material in spite of the small grain size in case of field assisted sintering. It may be due to the stresses spawning from uneven densification and transformation toughening dependence on the grain size. However, narrow distribution within the strength values of field assisted sintering showed that no large cracks are present, which may arise due to current density variations. This suggested that this technique can be used industrially for the production of symmetric or uni-shaped ceramic components.

In the end, it must be kept in mind that with the correctly manifested application of voltage and electric current processing temperature of ceramics can be lowered notably. Thus, it can lead to huge savings in energy with the additional benefit of low production cost as less expensive refractory material will be required for lower temperature

applications. With the advancement in these techniques one day, it may be possible to sinter ceramics together with metals.

4.2 Future Work

Based on the previous and current research being carried out following recommendations are suggested:

Comprehensive study of effects of external electric field on the intrinsic electric properties of ceramics compacts.

It would be interesting to see the mechanical testing results of yttria stabilized zirconia.

The Grain Growth Retardation Theory based on alteration of space-charge layer due to an externally applied field need deep and thorough studies. No physical evidence of such influence is present currently.

More such tests should be conducted on other insulating ceramics.

APPENDIX A

TiO₂ suspension Recipe Table:

	Vol %	Wt %	Weight used (g)	Volume used (ml)
Suspension	100			
Dry Content	11.12	31.38		
Powder	10.38		40.48	10.38
Dispersant wt% of Powder	2.44		3.95	2.96
water			86.66	86.66

APPENDIX B

Density Calculations for yttria-stabilized zirconia

*sample	M _d (g) Dry	M _w (g) In water	M _m (g) Moist	Open Porosity (%)	density(g/cm ³)	Relative density (%)
Tz 900°C	2.8818	2.403	3.3421	49.015	3.069	50.72
Tz 900°C,30v, 600mA	2.890	2.401	3.3418	48.4028	3.072	50.77
Tz 1000°C	2.8694	2.392	3.321	48.611	3.089	51.05
Tz 1000°C,30v,600mA	2.8732	2.3956	3.3185	48.250	3.113	51.46
Tz 1150°C	2.892	2.4134	3.2444	42.407	3.480	57.52
Tz 1150°C,30v,600mA	2.8529	2.3821	3.0257	26.849	4.433	73.27
Tz 1200°C	2.881	2.4088	3.1261	34.170	4.016	66.39
Tz 1200°C,30v,600mA	2.8792	2.3971	2.9681	15.569	5.042	83.35
Tz 1250°C	2.887	2.4107	3.0166	21.390	4.765	78.76
Tz 1250°C,30v,600mA	2.8823	2.3835	2.8967	2.806	5.616	92.83
Tz 1300°C	2.8739	2.3778	2.9104	6.853	5.396	89.19
Tz 1300°C,30v,600mA	2.8804	2.3859	2.881	0.121	5.818	96.16
Tz 1350°C	2.8901	2.3977	2.89	-0.020	5.871	97.03
Tz 1350°C,30v,600mA	2.8402	2.3673	2.8411	0.190	5.995	99.08
Tz 1400°C	2.8933	2.413	2.8942	0.187	6.013	99.38
Tz 1400°C,30v,600mA	2.9177	2.4326	2.9182	0.103	6.008	99.31
Tz 1500°C	2.8654	2.3939	2.8655	0.021	6.076	100.43
Tz 1500°C,30v,600mA	2.8635	2.3914	2.8634	-0.021	6.067	100.28
Tz 1200°C,30v,600mA (6mm dia.)	0.4036	0.3375	0.4087	7.163	5.669	93.69
Tz 1200°C,30v,600mA (12mm dia.)	1.714	1.44	1.77	16.970	5.194	85.95
Tz 1200°C,30v,600mA (20mm dia.)	4.5502	3.8008	4.8876	31.045	4.187	69.20
Tz 1200°C,35v,600mA	2.8933	2.4204	3.0651	26.648	4.488	74.18

* All the samples have same diameter of 16mm, otherwise mentioned.

Density Calculations for ceria-stabilized zirconia

*Sample	M _d (g) Dry	M _w (g) In water	M _m (g) Moist	Open Porosity (%)	density(g/cm ³)	Relative density (%)
ce zr green body	2.9293	2.4529	3.3219	45.178	3.371	53.934
ce 1000°C	2.9964	2.4552	3.3340	38.416	3.410	54.554
ce 1000°C 30v,280mA	2.9231	2.4495	3.3102	44.975	3.396	54.339
ce zr 1100°C	2.9023	2.4333	3.2000	38.829	3.785	60.567
ce zr 1100°C 30v,280mA	2.9265	2.4558	3.1971	36.503	3.948	63.165
ce zr 1150°C	2.9197	2.4478	3.1236	30.172	4.320	69.126
ce zr 1150°C 30v,280mA	2.9321	2.4611	3.0753	23.315	4.774	76.382
ce zr 1200°C	2.9165	2.4495	3.0238	18.684	5.078	81.254
ce ze 1200°C 30v,280mA	2.9211	2.4358	2.9320	3.321	5.831	93.299
ce zr 1250°C	2.9060	2.4048	2.9135	1.474	5.713	91.402
ce zr 1250°C 30v,280mA	2.9128	2.4347	2.9133	0.104	6.086	97.377
ce zr 1300°C	2.9174	2.4238	2.9174	0.406	5.922	94.759
ce zr 1300°C 30v, 280mA	2.9083	2.4356	2.9085	0.042	6.150	98.399
ce zr 1350°C	2.9167	2.4450	2.9168	0.021	6.182	98.913
ce zr 1350°C 30v,280mA	2.9011	2.4298	2.9059	1.008	6.093	97.495
ce zr 1400°C	2.9066	2.4397	2.9067	0.021	6.224	99.584
ce zr 1400°C 30v,280mA	2.9150	2.4428	2.9207	1.193	6.100	97.594

* All the samples have same diameter of 16mm.

APPENDIX C

Mechanical testing of ceria-stabilized zirconia

Conventional Sintering						
No	radius of the supporting circle (R1)	radius of the loaded area(R2)	Sample diameter (D)	Sample Thickness (t)	Breakdown Force (P)	Strength
	mm	mm	mm	mm	N	MPa
1	5	0.75	11.62	1.243	620	627
2	5	0.75	11.6	1.24	613	623
3	5	0.75	11.64	1.252	605	603
4	5	0.75	11.64	1.237	621	634
5	5	0.75	11.69	1.253	633	629
Average Value						623
Field Assisted Sintering						
1	5	0.75	11.62	1.253	618	615
2	5	0.75	11.63	1.237	575	587
3	5	0.75	11.59	1.232	601	619
4	5	0.75	11.6	1.231	569	587
5	5	0.75	11.63	1.245	612	616
6	5	0.75	11.59	1.23	570	589
Average Value						602
Standard Deviation						17.4706

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