Microstructural Characterization and Spark Plasma Sintering of BaTiO$_3$ Based Thermistors

A Master’s Thesis by

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Declaration

I, Maryam Karimi-jafari, hereby declare that the material within this thesis is the original product of my own research. All sources of information used as references and materials other than my own are duly acknowledged. This material has not been previously submitted to any University for any type of academic degree and has not been previously published.

____________________________________  ______________________________

Maryam Karimi-Jafari                   Date
Dedication

To my DAD, my first Love and my forever Hero.

You held my hand when I was small

You caught me when I fell,

The hero of my childhood and of latter years as well.

Every time I think of you, my heart just fills with pride,

And though I always miss you, Dad,

I know you are by my side.

In laughter and sorrow, in sunshine and in rain,

I know you are watching over me, until we meet again.
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Abstract

Barium titanate is one of the most important and widely studied ferroelectric ceramics with ABO$_3$ type perovskite structure. Due to its promising ferroelectric properties, it has been used in several applications such as positive temperature coefficient resistors (PTCR) called thermistor, sensors, electro-optical devices, multi-layer ceramic capacitors (MLCCs), electroluminescent panels, etc. Barium titanate shows a significant phase transition below and above Curie temperature (120 °C for pure barium titanate) from tetragonal to the cubic crystal structure. This phase transition however is strongly dependent on the microstructural properties such as density, grain size distribution, type of dopants and sintering conditions. In this research, extensive characterization techniques such as X-ray diffraction (XRD), scanning electron microscopy (SEM), Raman spectroscopy, electron backscattered diffraction (EBSD), and energy dispersive X-ray spectroscopy (EDX) were used to study the microstructural and compositional characteristics of 8 industrial samples. We have employed state of the art spark plasma sintering that offer rapid consolidation of powders, enabling significantly improved or even completely novel materials on barium titanate samples containing Ca, Sr and Pb as a dopant. The effect of various sintering parameters e.g. sintering temperature, soaking time and heating rate on microstructural and phase composition of the sintered samples were investigated and compared to the benchmark industrial sample.
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List of Publication

Book Chapter:

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Chapter 1 : Introduction

1.1 Introduction

Since the discovery of the ferroelectricity in polycrystalline barium titanate in the mid-1940s it has attracted lots of attentions due to its high dielectric constant and low loss characteristics. It has found several applications such as capacitors, multilayer capacitors and energy storage devices[6]. Barium titanate has found several applications as semiconductors, positive temperature coefficient resistors (PTCs)[7], and piezoelectric devices[8].

Spark Plasma Sintering (SPS) is a novel sintering method using simultaneous high pressure and temperature in order to produce high-density materials with low exaggerated grain growth, and high mechanical strength. This method has also been used for sintering of barium titanate and other ferroelectric ceramics[9]. The effect of various sintering parameters on the microstructural and phase composition of the sintered ferroelectrics has shown to be critically important for their functional properties[10].

The objective of this research is to study the microstructure and phase composition of the several industrially provided barium titanate PTC stones using extensive characterisation methods such as scanning electron microscopy (SEM), electron backscattered diffraction spectroscopy (EBSD), energy dispersive X-ray spectroscopy (EDX), X-ray diffraction (XRD), atomic absorption spectroscopy (AAS), Raman spectroscopy and electrical measurements. For further investigations, SPS was employed as a novel sintering method to study the effect of various sintering
parameters such as sintering temperature, soaking time and heating rate on the microstructural and phase composition of the barium titanate samples.

1.2 Research Questions

The questions that this research project is going to answer are as follows:

1. What are the microstructural and compositional characteristics of industrial PTC stone?

2. What are the effects of various sintering parameters (heating rate, sintering temperature and soaking time) on microstructural and compositional characteristics of sintered barium titanate samples?

1.3 Research Hypothesis

The above research questions were addressed on the basis of the following research hypothesis:

1. Characterisation techniques provide important details about the microstructural and phase compositional of the industrial samples.

2. It is possible to control the microstructural and phase composition properties of doped barium titanate with spark plasma sintering (SPS).
1.4 Methodological Approach

This section outlines the experimental procedure employed during this research project. Figure 1.1 shows the flowchart of the outline of each step taken. Sample D was chosen as benchmark because it had the lowest divergence of resistivity measurements among all other industrial samples.

![Flowchart of the methodological approach](image)

**Figure 1.1.** The outline of the methodological approach applied in this research project.

1.5 Scope of the Thesis

In this section a summary of the addressed issues in every chapter is provided as follows:
Chapter 1: Introduction

This chapter introduces the background, research questions and research hypothesis. Also, a summary of the research methodology is provided.

Chapter 2: Literature Review

This chapter addresses the literature with introducing ferroelectric ceramics and specifically barium titanate. Also, different methods of synthesis and sintering of barium titanate are reviewed.

Chapter 3: Methodology

This chapter discusses the various characterization techniques such as SEM, EDX, EBSD, XRD, Raman spectroscopy, and AAS used in this study. Furthermore, the sample preparation method for e.g. the powder synthesis and spark plasma sintering are explained.

Chapter 4: Structural characterisation of PTC stones

This chapter describes the results of all the characterisation techniques (microstructural, phase and elemental composition) mentioned in chapter 3 for the industrial PTC stones.

Chapter 5: Spark plasma sintering of BaTiO₃

This chapter describes the effect of three sintering parameters of heating rate, temperature and soaking time on microstructural and compositional characteristics of the barium titanate samples.

Chapter 6: Conclusion
This chapter summarizes the findings of this study. Also, it addresses the research questions mentioned in chapter 1. Finally, it presents recommendations for future work.
Chapter 2 : Literature Review

2.1 Introduction

In this chapter, a review on ceramics and electroceramic materials is provided. Also, different polarizations in electroceramics are presented. Barium titanate as a ferroelectric ceramic is introduced and its applications, synthesis procedures and effective parameters are stated. Also, the literature was investigated to clarify the effect of different sintering techniques and their parameters and dopants on microstructural characteristics of barium titanate.

2.2 Ceramics and Electro Ceramics

The word ceramic is originated from Greek word of keramos which used to call materials were made of clay and fired. Also, it can be called ‘pottery’ which is mainly based on clay and other siliceous minerals. That is why clay is mouldable while mixed with water and it can maintain its shape after drying. Furthermore, its mechanical strength is increased after firing. The potteries are the first examples of ceramic materials. The advanced ceramics are regarded as to a broader range of materials. These materials are described as ‘solids that their essential components are inorganic non-metallic materials’[11]. Ceramics, by definition, show ionic contributions in their chemical bonds which include inorganic, non-metallic and non-water-soluble compounds. The technical exploitation of ferroelectric ceramics began after the Second World War. They have unique properties such as high piezoelectric constants and electromechanical coupling ,high dielectric permittivity, high pyroelectric coefficients and under certain conditions high optical transparency and electro optic coefficients[12].
The first electrical uses of ceramics were related to their electrical insulation property; ceramics due to their high mechanical strength, environmental stability and high electrical resistance were used in insulations for electrical cables. Ferrite was also widely used for radio receivers in the period of 1930-1950. It was only from 1920 that conductive ceramic came into the market. For instance, ceramics with the high negative temperature coefficient of resistivity were used as temperature indicators. High permittivity dielectrics based on barium titanate have emerged in the 1940s which revolutionized the applications of ceramics in transistors. Also, sintering of barium titanate in reducing atmosphere leads to high positive temperature coefficient (PTC) resistors as the resistivity increases over a narrow range of temperature. This happens because of the transition from ferroelectric to paraelectric state [6, 8, 11].

### 2.2.1 Polarization in Ceramics

In ceramic crystals with ionic structure, the electrons are tightened firmly to the core. In normal temperature electrons cannot be separated but by applying an electric field, the situation can be changed. It should be mentioned that when electric field causes electric charges polarization, positive charges move in the same direction with electric field whereas, negative charges shift to exact opposite direction. This movement leads local dipoles so electric polarization occurs [13].

#### 2.2.1.1 Dielectric Ceramics

Dielectrics can be described as a high electrical resistance materials[11] and they are ceramics which has good electrical insulation. When an electrical field is applied, dielectrics will not allow the current to pass through easily. However the applied electric field causes a slight shift in the balance of charge within the material so the
system acquires a dipole moment which is referred to as polarization; the polarization can be defined as a dipole moment per unit volume[1]. Figure 2.1 shows polarization in dielectrics.

\[ E = 0 \]

\[ \rightarrow E \]

![Figure 2.1. Polarization in dielectric materials [13].](image)

In terms of dielectricity there is a constant which shows the degree of polarizability or charge storage capability of a material and it is called dielectric constant or relative permittivity. When electrical field is applied to two flat pieces of metal, one of them will have a positive charge and the other one negative charge so electric field can create a polarization for the material which is between these two conductive metal pieces. Dielectric constant is the ratio of the polarizability of dielectric material to vacuum between two metal pieces [1]. Figure 2.2 shows this concept simply.
Barium titanate is the first material applied for manufacturing of dielectric ceramic capacitor which Table 2.1 presents the barium titanate dielectric constant with various synthesis methods[8]. Erie Resistor Company measurements showed that barium titanate has permittivity 10 times more than other ceramics which had been found at that time[14].

\[
k' = \frac{K_{\text{material}}}{K_{\text{vacuum}}} \]

Figure 2.2. Schematic presentation for illustration of dielectric constant.
Table 2.1. Dielectric constant of BaTiO3 obtained with a different synthesis routes[8].

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<th>Method of synthesis</th>
<th>$T_s$ (°C)</th>
<th>Dielectric constant (k) at $T_{room}$</th>
<th>Dielectric constant (k) at $T_{Curie}$</th>
<th>Frequency</th>
</tr>
</thead>
<tbody>
<tr>
<td>Arya et al.[15]</td>
<td>Sol-gel</td>
<td>1200/1300 20 min</td>
<td>500-650/700-900</td>
<td>-</td>
<td>1MHz</td>
</tr>
<tr>
<td>Boulos et al.[16]</td>
<td>hydrothermal</td>
<td>1250/2h</td>
<td>2000</td>
<td>7000</td>
<td>1kHz</td>
</tr>
<tr>
<td>Xu et al.[17]</td>
<td>hydrothermal</td>
<td>900/2h</td>
<td>6900</td>
<td>11000</td>
<td>-</td>
</tr>
<tr>
<td>Vinothini et al.[18]</td>
<td>Pechini</td>
<td>1300/3h</td>
<td>1700</td>
<td>2840</td>
<td>1kHz</td>
</tr>
<tr>
<td>Guillemet et al.[19]</td>
<td>Pechini</td>
<td>1260/1-5h</td>
<td>$\geq$5000</td>
<td>10000</td>
<td>1kHz</td>
</tr>
<tr>
<td>Stojavonic et al.[20]</td>
<td>mechanochemical</td>
<td>1330/2h</td>
<td>2500</td>
<td>7500</td>
<td>100kHz</td>
</tr>
<tr>
<td>Buscaglia et al.[21]</td>
<td>precipitation</td>
<td>1310/*</td>
<td>665</td>
<td>880</td>
<td>10kHz</td>
</tr>
<tr>
<td>Seveyrat et al.[22]</td>
<td>Oxalate coprecipitation</td>
<td>1350/4h</td>
<td>2200</td>
<td>8000</td>
<td>1,10,100 kHz</td>
</tr>
</tbody>
</table>

2.2.1.2 Piezoelectric Ceramics

The name “piezo” is a Greek word which means “press” so piezoelectricity is the electricity generation as a result of a mechanical pressure and this property was discovered in 1880 by Jaques and Pierre Curie when they were studying the effect of pressure on electrical charge production in crystalline materials[6]. Some certain crystalline materials are able to develop an electrical charge proportional to a mechanical stress which is defined as a piezoelectricity [23]. Thus, piezoelectric materials can make a link between mechanical and electrical properties which they can convert to each other. It should be mentioned generally, more piezoelectric coefficient provides more efficiency in applications. Only anisotropic crystals with no center of symmetry are piezoelectric so among 32 crystal classes just 20 of them shows
piezoelectricity[24]. It should be noted that piezoelectricity is a kind of reversible and linear phenomena that 2 factors have a direct effect on it: 1) stress magnitude define the polarization amount and 2) sign of the generated charge depends on a stress type (tensile or comprehensive)[6]. Figure 2.3 shows a schematic for piezoelectric material.

According to the Figure 2.4 in the class of ferroelectric material, there are four subgroups: perovskite group, pyrochlore group, tungsten-bronze group and bismuth layer structure group. Among all four, the perovskite group is the most applicable and highly focused materials [25]. Usually, perovskite structure is shown by ABO$_3$ such as BaTiO$_3$ which will be discussed in section 2.2.1.4.1 and Figure 2.7.
2.2.1.3 Pyroelectric Ceramics

Pyroelectricity is the electrical response of polar, dielectric material to a change in temperature. In other word, pyroelectricity provides one of the best performing
fundamentals for the detection of temperature changes. Pyroelectricity happens in polar materials. There is an equation which shows this relation simply [26]:

$$\Delta Q = Ap\Delta T$$  \hspace{1cm} (2.1)

In basic structure, $Q$ is a charge of the planar capacitor, $T$ is temperature, where $A$ is capacitor area and $p$ shows pyroelectricity coefficient.

When temperature changes in dielectric material, the response will be an electrical charge which called pyroelectricity. It is based on polar features which lined up in the same direction. From the structural point of view, pyroelectricity happens in crystalline symmetric materials that can have a polar direction. Previously, mentioned that only 20 of crystal classes show piezoelectricity and now it should be noted just 10 of them are polar and potentially can be pyroelectric. Hence, all pyroelectric materials are piezoelectric but the converse is by no means true [26]. In rest of the piezoelectric materials (non-polar) the polarization is detected by applying a mechanical load.

Figure 2.5 shows a schematic for pyroelectric material.

![Figure 2.5. Schematic representation of pyroelectric materials.](image)

2.2.1.4 Ferroelectric Ceramics

Ferroelectricity was discovered in 1921 for the first time. The prefix “ferro” is a Greek word and means iron. Most of the ferroelectrics do not contain iron and using of this term is related to similarity between ferroelectrics and ferromagnetic properties of
iron. The intrinsic behaviour of ferroelectrics is showing spontaneous polarization even in the absence of an applied electrical field. Ferroelectrics are a subgroup of pyroelectrics which preserve their polarization even after an applied electric field has been removed[1]. All ferroelectrics have a temperature that spontaneous polarization changes below and above it. This point is called Curie temperature or Curie point. When temperatures are higher than Curie temperature, the electrical polarization of materials is diminishes extensively so the crystal will be electrically neutral. This crystallographic phase is called paraelectric. Below the Curie temperature, the crystal is spontaneously polarized and this crystallographic phase is called ferroelectric. Curie point plays a major role in ferroelectrics behaviour[27]. Subsequently, the temperature of phase transition is called Curie temperature. Range of this point is wide and it can be lower than liquid nitrogen temperature or higher than 1000°C for different materials. The Curie point can be explained by Curie-Weiss law which shows how the dielectric constant ($\varepsilon$) decreases sharply at this temperature ($T$)[28]:

$$\varepsilon = \varepsilon_0 + \frac{C}{(T-T_c)}$$

(2.2)

Where, $\varepsilon_0$ is the dielectric constant of free space, $C$ is the Curie-Weiss constant and $T_c$ is the Curie temperature. Curie temperature is closely dependent on microstructure such as grain size distribution, porosity, density and impurity. It can be claimed generally the smaller grain size, the lower Curie temperature[25].There are 2 main circumstances which define a material as a ferroelectric: 1) presence of spontaneous polarization 2) confirmed reorienting of the polarization so it is clear that all ferroelectrics are piezoelectric but all piezoelectric are not ferroelectric. The figure illustrates a schematic for ferroelectric materials.
2.2.1.4.1 Barium titanate

Barium titanate is one of the most famous ferroelectric ceramic material with ABO$_3$ type perovskite structure[29]. Due to brilliant dielectric, ferroelectric and piezoelectric properties of barium titanate, it was synthesized to become the first and the most extensively studied ceramic material [27]. Ferroelectricity of barium titanate was discovered on the 1940s. It is widely applied in different types of electronic components such as positive temperature coefficient resistors (PTCR) called thermistor, sensor, electro-optical devices, multi-layer ceramic capacitors (MLCCs), electroluminescent panels, pyroelectric elements, polymer matrix composites for embedded capacitance in printed circuit boards, heater, fuel evaporators, air conditioning equipment and transducers [30],[29].

Perovskite structure has typical composition ABO$_3$, where B is matched by oxygen octahedrally and A is 12 fold coordinated with respect to oxygen. As Figure 2.7 shows there are two possible positions for A and B, one structure is having A site on the corner of cube, B site at the centre and oxygen at the middle of each face or second structure is converse, means A site is at the centre, B site is on the corner and O ions at the midpoint of each edge[31].

Figure 2.6. Schematic of ferroelectric materials.
BaTiO$_3$ has five different crystal structures: hexagonal, cubic, tetragonal, orthorhombic, and rhombohedral. The hexagonal and cubic structures are paraelectric while the tetragonal, orthorhombic and the rhombohedral forms are ferroelectric in nature. Figure 2.8 shows these phase transition for barium titanate in different temperature [1].

Figure 2.7. Perovskite crystal structure of barium titanate (a) Cubic paraelectric structure of barium titanate, (b) ferroelectric tetragonal structure of barium titanate [1].
Crystallographic structure of barium titanate shows strong temperature dependence. If temperature decreases below 130°C, structure will transform from cubic to tetragonal so at room temperature barium titanate structure is tetragonal. The temperature where cubic to tetragonal transformation takes place is called Curie temperature.

It should be noted that barium titanate will maintain its tetragonal structure until 0°C and below this temperature, it transforms to orthorhombic form. Tetragonal phase structure shows a distinctive splitting of certain peaks at 45 degree in X-ray characteristic pattern. Hence, X-ray diffraction spectroscopy (XRD) is a significant

Figure 2.8. Barium titanate phase transition with temperature[2].
method to determine the crystal structure of barium titanate[32]. At Curie point, during the transformation of paraelectric phase (cubic) to ferroelectric phase (tetragonal) uniform polarization regions which is called ferroelectric domains will be formed. In each domain, electric dipoles are aligned in the same direction. The interface can separate domains from each other is named domain wall[33]. Two factors can change the type and configuration of domains: the existence of dopant and microstructure gained during the sintering process. In terms of achieving uniform, ferroelectric behaviour of barium titanate should be noted, homogeneous and small grained structure with a single domain can cause stability[8]. Maximum alignment of the domain is achievable by cooling the barium titanate through Curie temperature[1].

The commonly accepted criterion of ferroelectricity is a hysteresis loop on a polarization (P) - electric field (E) display. In terms of Barium titanate hysteresis loop it should be noted that there is a close relation between hysteresis loop shape and temperature. Stojavonic et al. studied the hysteresis loop for barium titanate at room temperature and they observed a well-defined loop with regular shape typical for ferroelectric material as shown in Figure 2.9, the remnant polarization was $2.0 \, \mu \text{C/cm}^2$ and the coercive field was 1060 kV/cm.[20].
When the temperature decreases and goes below room temperature the hysteresis loop will be wider this is because of the larger amount of energy is needed to reorient the domain walls so coercive field value will be more.

As the temperature increases the coercive field becomes smaller consequently at Curie point no hysteresis loop remains and dielectric constant will have a single value[34]. Figure 2.10 illustrates these changes for barium titanate.

Figure 2.9. The hysteresis loop for barium titanate at room temperature[1].

Figure 2.10. Dependence of hysteresis loop with temperature in barium titanate[1]
2.2.1.4.2 Application of Ferroelectric ceramics

Ferroelectric materials are major electronic substances that they are highly applicable in industrial and commercial fields such as high-dielectric-constant capacitors, piezoelectric sonar, ultrasonic transducers, pyroelectric security sensors, medical diagnostic transducers and electro-optical light valves and ultrasonic motors[25]. The most famous ferroelectric material are barium titanate BaTiO$_3$, lead zirconate titanate Pb(Ti,Zr)O$_3$ (PZT), lead titanate (PbTiO$_3$), lead lanthanum zirconate titanate (PLZT), LiNbO$_3$, KNbO$_3$, LiTaO$_3$, Pb(ZnNb)O$_3$ and lead magnesium niobate (PMN). These materials have been improved via extensive research in the field and applied for different kind of applications because of their common property having a high dielectric constant[35]. There are several applications for resistors with high values of the temperature coefficient of resistance (TCR) and they can have negative temperature coefficient (NTC) or positive temperature coefficient (PTC) resistor which will be discussed further in the coming sections[11].

2.2.1.4.2.1 Negative Temperature Coefficient (NTC) resistor (NTC thermistor)

In this type of resistors with increasing temperature, the resistance will decrease and this change is drastic at Curie temperature so they called Negative Temperature Coefficient (NTC) resistor[11]. Many required features for temperature measurements have been offered by NTC thermistors. The word “thermist” is derived from THERMally sensitive resiSTOR[36]. Advantages of applying NTC thermistor include fast response time, low cost, small size and large changes in resistance versus temperature. NTCR thermistors are finding an increasing number of applications in medical procedures, home appliances and industry such as portable consumer electronics, audio and video equipment and power tools[37].
2.2.1.4.2.2 Positive Temperature Coefficient (PTC) resistor (PTC thermistor)

Positive temperature coefficient thermistors behave inverse the NTC thermistors. They can be classified as a thermo-sensitive materials whose resistivity stay constant at low temperature but increases sharply at Curie point [38]. This effect was first detected in 1950’s in Philips Research Laboratories in Netherland [39]. In these materials, an anomalous increase in electrical resistivity happen near the ferroelectric-paraelectric Curie transition temperature. PTC thermistors have a wide variety of applications such as heating elements, integrated circuits and temperature sensors[40].

In fact, the PTC materials can be divided in four groups: polymer composites, ceramic composites, V$_2$O$_3$ composites and BaTiO$_3$-based compounds (BaSrTiO$_3$, BaPbTiO$_3$, etc.) [41]. The role of various dopants on the PTC effect in barium titanate ferroelectrics have been studied extensively during last five decades. For example, Curie temperature can be increased by adding Pb and reduced by adding Sr as dopants [42]. Jingchang Z et al. studied the effect of adding PbO and SiO$_2$ on properties of Sr$_{0.4}$Pb$_{0.6}$TiO$_3$ and they showed that PbO dopants decreases the resistivity at room temperature but SiO$_2$ has a reverse effect [43]. Figure 2.11 shows this trend.
Also, the PTC effect of doped barium titanate is highly dependent on firing conditions. It has been shown that pure stoichiometric barium titanate which is an insulator at room temperature after sintering in air, becomes a semiconductor by sintering in nitrogen atmosphere at 1450 °C and finally quenching [44]. It has been stated that the loss of oxygen from the barium titanate structure happens gradually during the sintering process which leads to increase in electrical conductivity. So, providing a reducing atmosphere can enhance the conductivity of doped barium titanate [45, 46]. Therefore, methods such as spark plasma sintering (SPS) which provide a relative vacuum during sintering process can be helpful in this regard.
Syrtov S.R. et al. showed that resistance of $100(Ba_{0.92}Ca_{0.08})TiO_3+0.35Y+1.0SiO_2$ thin films will be increased in temperature range 50 °C to 80 °C which is a good prove for PTC effect [40]. (Figure 2.12)

![Figure 2.12. Typical resistance behaviour of ferroelectric film [31].](image)

2.2.1.4.2.3 Multi-Layer Ceramic Capacitors (MLCCs)

There are different types of ceramic capacitors but multi-layer capacitors have the largest quantity and importance in terms of production. It is estimated that the number of MLCC pieces used in mobile phones is 150, in PDA (Personal Digital Assistant) is 200, and in digital TV set is around 300 [47]. A simple pattern for the multi-layer capacitor can be fabricated by a pair of parallel metal plates which are separated by a free space between them. When a voltage is applied on the metal plates, electrical charge starts to develop; the charge amount is dependent on the applied voltage.
The charge on the plates can be increased by putting an insulator between these parallel metal plates because dielectric constant of the insulator has a direct impact on the charge. Regarding high dielectric constant of BaTiO$_3$, it has been used widely as dielectric in capacitors. Increasing the dielectric constant of dielectric materials leads to increase in capacitance of the capacitor. The first MLCCs were introduced in the early part of World War II[11]. The multilayer capacitor structure enables the maximum capacitance available from a thin dielectric to be packed into the minimum space in a mechanically robust form[48].

Recently further improvements have been demonstrated in MLCC technology and now nickel (Ni) and copper (Cu) internal electrodes have been replaced with Ag-Pd electrodes which have huge advantages on manufacturing cost. The production rate of MLCCs with nickel internal electrodes that are composed of 500 or more laminated thin dielectric layers of ~2 µm is increasing[49].

2.3 Methods of Synthesis

2.3.1 Solid State Synthesis Route (SSS)

Generally, all solid state reactions are based on the formation of product phases at the interfaces of reactants[50]. Regarding efficiency, the best method to activate reactants mechanically is grinding in the close volume. The grinding media is chosen to be harder than the materials intended to be milled [51]. In terms of powder preparation of ceramics, solid state reaction can be a good method because it starts with intensive milling in the high-energy milling machine. Intensive milling can enhance the surface contact between the reactants powder particles because during the milling process particle size will be decreased. Generally solid state reaction needs high temperature
to activate the reactants. After growing of product phase, diffusion will happen and then some layers will be appeared which will block the diffusion path of reactants. Hence, reaction speed will be decreased. Consequently, one benefit of mechanochemical synthesis is the ability to activate the reactants in lower temperature[50].

It was shown that mechanochemical method is an expedient way to synthesise polycrystalline pyro, piezo and ferroelectric ceramics [52-55]. This method is advantageous for barium titanate production too. Also, it was noted that sintering will be progressed due to the mechanical activation of initial powder of BaCO$_3$ and TiO$_2$ [50]. Due to the synthesis of BaTiO$_3$, T. Kozawa et al applied solid state reaction without mechanochemical processing in water vapour atmosphere. Calcination at 700 ºC for 4 h produced single phase of Barium Titanate and water vapour atmosphere was helpful to speed up the formation rate. They calcined Barium titanate at 850 ºC for 2.5 h in air atmosphere to complete the reaction. Also, they showed that particle size of synthesized barium titanate in water vapour atmosphere by calcination at the lower temperature and shorter time is the same or smaller than those obtained in air atmosphere [56]. B. D. Stojanovic et al. also used mechanochemical synthesis in a planetary ball mill in air atmosphere. They reported that the synthesis was started after 60 minutes and highly crystalline barium titanate powder was achieved after 240 minutes [50].

2.3.2 Effect of Dopants or Additives on BaTiO$_3$ Properties

Electrical and microstructural properties in BaTiO$_3$ based ceramics are strongly dependent on composition and microstructural development. Normally BaTiO$_3$ is not used as a pure one by itself in industrial application such as PTC thermistors. Owing to different applications of this ceramic, usually various materials are added to
improve the properties in certain respects[57]. Different additives such as Ca$^{2+}$, Sr$^{2+}$ ions at A site and/or Zr$^{4+}$, Mn$^{4+}$, Nb$^{5+}$, Fe$^{2+}$ ions at B site are known to shift the phase transformation temperature in BaTiO$_3$. As a result, these dopants can suit BaTiO$_3$ for piezoelectric devices[58]. D.VÖltzke et al. showed that different mechanism of adding Ca causes different properties for BaTiO$_3$. They present 2 series called series C and series H. In series C, CaCO$_3$ was used as a Ca source but in series H, ceramics prepared via hydrothermal Ca modification. In electrical characteristics (resistivity in room temperature 20ºC and voltage withstanding (E)) both series are shown in Table. The resistivity measurements with x=0.04 depict a steeper drop of resistivity above the Curie temperature in series H. In series C, voltage withstanding will be increased to 60 V/mm only if Ca is 12±16 mol% but in series H, the value of E is reached with only 4 mol% of Ca. In summary, Ca is added for a grain refining effect[57].

**Table 2.2.** Voltage withstanding $E$ and resistivity at room temperature $\rho_{20}$ of Ca-modified ceramics, $La_{0.002}Ba_{0.998-x}Ca_xTi_{1.01}O_{3.02}$, sintered at 1350ºC[57]

<table>
<thead>
<tr>
<th></th>
<th>Series C</th>
<th></th>
<th></th>
<th>Series H</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca content x (mol %)</td>
<td>E (V/mm)</td>
<td>$\rho_{20}$ (Ωcm)</td>
<td>Ca content x (mol %)</td>
<td>E (V/mm)</td>
<td>$\rho_{20}$ (Ωcm)</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>8.4</td>
<td>17.8</td>
<td>0</td>
<td>14.3</td>
<td>15.3</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>11.2</td>
<td>20.9</td>
<td>4</td>
<td>58.5</td>
<td>174</td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>44.2</td>
<td>41.1</td>
<td>8</td>
<td>68.4</td>
<td>342.6</td>
<td></td>
</tr>
<tr>
<td>16</td>
<td>60.5</td>
<td>892</td>
<td>16</td>
<td>32.4</td>
<td>48.8</td>
<td></td>
</tr>
</tbody>
</table>
A-site substitutions of Sr or Pb are commonly added to control the switching temperature $T_C$ [59].

The addition of Sr as a dopant to barium titanate increases the dielectricity. Moreover, Sr can control the transition temperature[60]. M. Sindhu et al proved that when Sr is increased a linear decline in Curie temperature and tetragonality is observed[61]. Figure 2.13 shows temperature and composition dependence of dielectric constant ($\varepsilon'$) for all the samples at 100 kHz for (BST) $\text{Ba}_{1-x}\text{Sr}_x\text{TiO}_3$ (BST, $x = 0.05, 0.10, 0.15$) [61].

![Figure 2.13](image)

**Figure 2.13.** Temperature and composition dependence of dielectric constant ($\varepsilon'$) for all the samples at 100 kHz.

Lead has opposite effect on $T_C$ in comparison to Sr but normally they are both added to the commercial samples as dopant. Lead can enhances liquid phase at lower sintering temperatures and Sr compensate these changes in $T_C$ caused by adding Lead[57].
2.4 Sintering of Ceramics

2.4.1 Sintering methods and procedure

Sintering can be defined as a consolidation process for powders which refers to 6000 years ago when the human tried to make bricks and pottery. Sintering is a valuable method because it is able to consolidate powder without melting. This process is achieved because of the reduction of the grain boundaries and surface energies during sintering which are used as a driving force for thermal activation. To achieve dense samples and optimize the thermal activation, sintering can be done in higher temperature according to the melting point of materials. For saving time and energy lots of efforts are being done to decrease the temperature and time for sintering[62]. During sintering, processes such as burn out of the solvents which were used as a binder to form compressed powder and phase transformation can happen. Because of this complexity, the process should be controlled via multi-staged heating profile. The sintering process is often divided into steps as presented on Figure 2.14.
The first step in sintering process is the burnout of the binder by slow heat up. Duration of this stage depends on the size of sample and binder amount. Next stage is low-temperature soak at which modification of microstructure is accomplished. At this stage, chemical homogenization like solid-state reaction or liquid phase formation possibly will happen. The third step includes heating up the sample to reach the sintering temperature. There is a critical factor in the third stage which is heating rate, as the higher the heating rate, the more the densification happens[63]. Since the grains are exposed to higher temperature for less time, they do not have enough time to grow therefore their size will be smaller. At fourth stage final densification will occur due to isothermal sintering. At this step, there are two important parameters; the sintering duration (also called holding time) and sintering temperature that effect the grain coarsening and hence cause abnormal grain growth. In order to achieve proper chemical homogenization, sintering time and temperature needs to be properly controlled. Next or second last stage is the cooling down the temperature to room temperature. It may happen in some cases, during the cool down process an extra step.
is needed calling annealing. Annealing can be helpful in terms of reduction of thermal stresses within the sample. Depending on the sample size, cooling rate will be different. For instance, bigger samples need slower cooling rate because fast cooling down can cause cracks within the sample. Subsequently, smaller samples can have faster cooling rate. Hence, to accomplish good structural modification, cooling rate should be controlled [63]. Diffusion is also a big factor for mass transfer during the sintering of crystalline solids. There are 2 factors that can change diffusion: 1) temperature 2) defect concentration, therefore by diffusion control sintering can be managed. Moreover, pressure plays a big role in sintering so sintering can be classified in two main groups: pressure sintering such as Spark Plasma Sintering and pressure less or free sintering such as Conventional sintering and Microwave sintering which will be discussed in the next sections [63].

2.4.1.1 Conventional Sintering
This method is used in sintering of conventional ceramic bodies. Simple box furnaces and tube furnaces can be used for conventional sintering. In this method, heat will be transferred to the sample by 3 mechanisms: 1) Conduction 2) Radiation 3) Convention. According to these heat transfer mechanisms, the heat transfer rate cannot reach to high values. Also, the cooling rate in this method cannot be controlled accurately. During the heating of the sample in conventional sintering, some temperature gradients between inside and outside will be generated because first, surface will start to heating up and then heating moves inwards. Sample preparation for conventional sintering includes mixing, milling and pressing the powder to a green body. Different types of furnaces are applied for conventional sintering such as electrical resistance furnace, fossil fuel furnace and induction furnace that all of them use a large amount
of energy and it is not cost-effective[64]. Figure 2.15 shows the simple schematic of heating transformation in conventional sintering.

![Schematic of heating transformation in conventional sintering](image)

**Figure 2.15.** Schematic of heating transformation in conventional sintering

2.4.1.2 Microwave sintering

Microwave energy is a kind of electromagnetic energy which has the range between 300MHz and 300GHz. In the microwave sintering process, first the material absorbs electromagnetic energy and then converts it to heat. In this method heating process is different from conventional, first inside of sample will be heated up then it spreads in the whole volume. Because of this heating mechanism microwave sintering has lots of advantages over the conventional such as higher heating rate, lower sintering temperature, more diffusion, better mechanical properties and lower energy consumption[64]. It was reported that microwave sintering of barium titanate in comparison with conventional sintering can achieve a faster densification at lower temperature because microwave field can increase bulk diffusion instead of grain boundaries diffusion[65]. Figure 2.16 shows a simple schematic of heating transformation in microwave sintering process.
2.4.1.3 Spark Plasma Sintering (SPS)

SPS can be defined as a fast process which in lower temperature can reach higher densification in only a few minutes in comparison with conventional and microwave sintering which take hours. In this method pulsed direct electrical current pushed through the sample together with high uniaxial pressure at low atmospheric pressure leads to rapid densification of powders. SPS applies temperature and pressure simultaneously and it causes higher densification in lower temperature (200-250 °C) lower than conventional sintering temperature. The dielectric and ferroelectric properties of materials will be improved during the SPS [66]. Hot Isostatic Press (HIP) method uses temperature and pressure at the same time like SPS but the heating rate in SPS is really higher than HIP so undesired grain growth will be decreased significantly[66]. The development approach of Field-Assisted Sintering Techniques (FAST) and Pulsed Electric Current Sintering (PECS) is getting more efficient powder consolidation so SPS has appeared as a great replacement for conventional sintering. Figure 2.17 illustrates the simple schematic of SPS machine and it consisted of: two graphite punches (upper and lower), one graphite die, uniaxial pressure, vacuum chamber and integrated water cooling system and SPS controlling system[67].

![Figure 2.16. Schematic of heating transformation in microwave sintering](image-url)
2.4.1.3.1 Sintering mechanism of SPS

Sintering mechanism usually consists of 4 main steps: 1) powder refining and activation 2) neck formation 3) neck growth and 4) plastic deformation densification. In SPS, electrical discharge can remove the oxidations on the surface of particles so neck formation will be simplified between particles. It is believed that voltage breakdown can control the step 1 and step 2 in SPS sintering. In addition, Pressure and Joule effect (the heating that happens when an electric current flows through a
resistance) can control the step 3 and step 4 because of their effect on increasing the neck growth and final densification[68]. During the sintering, the formed liquid phase enhances the rate of sintering and applied pressure is able to rush the densification process and eliminates the residual pores. The mass transport mechanism for the majority of inorganic powder consist of: surface diffusion, volume diffusion, grain boundary diffusion, dislocation climb, viscous flow, plastic flow, solution-reprecipitation and even vapour transport from the solid surface[69].

![Figure 2.18. Sintering mechanism.](image)

2.4.1.3.2 SPS of BaTiO$_3$

SPS has shown to be superior compared to conventional sintering due to its fast, high pressure and highly controllable process [70]. In this method, sample preparation involves 4 steps: synthesis of powder, powder preparation (grinding/ball milling), sintering and annealing at the lower temperature for a longer time[71]. In conventional sintering, slow heating rates lead to high grain growth, while in SPS method, uniform heating condition, shorter sintering time and lower sintering temperature usually leads
to lower grain growth and smaller grain size. Overall SPS can compensate the limitations of conventional sintering method [70]. SPS compared to conventional sintering has lots of advantages such as hot-pressed sintering and high heat efficiency. SPS by exploiting pulse energy, spark pulse pressure and Joule heating produce a high-temperature field. In conventional sintering, heating source is external but in SPS instead of that, pulsed DC current is applied which passes through the pressure die as well as the sample. This process helps sample to be heated both internally and externally. SPS provides a situation that the interior surfaces of the grains are heated while the exterior surfaces are excited simultaneously by spark plasma. All above mentioned, improve diffusion rate and increase the densification of the final product [72]. These are the advantages of SPS over conventional sintering method.
Chapter 3  : Methodology

3.1 Introduction

In this section, characterization methods of industrial samples are described in detail. Also, the sintering procedure of new specimens based on the best performed industrial sample is stated. Eight commercial PTC thermistor samples labelled as (A-B-C-D-E-F-G and H) were chosen for this study. The samples have Barium Titanate (BaTiO$_3$) as main materials with addition of different dopants and use Aluminium (Al) as a conductive layer on top and bottom face of each pellet. The elements such as Calcium (Ca), Strontium (Sr) and Lead (Pb) were added to these samples as dopants. In terms of electrical properties and PTC effect sample D showed the best performance. The properties of each pellet were characterized and compared with replicates prepared via SPS sintering. Various analytical methods such as morphological characterization and surface characterization were applied to analyse the properties of each pellet. Grain size distribution is analysed using the SEM images of the samples. X-ray diffraction (XRD) was employed for recognition of crystal structure and phase composition of each pellet. Energy Dispersive X-ray spectroscopy (EDX) was used for finding the composition of surface and bulk. Scanning Electron Microscopy (SEM) was exerted to study the morphology of microstructure. Atomic Absorption Spectroscopy was applied for measuring the concentration of dopants in each batch precisely.
3.2 PTC stones characterisation

3.2.1 Sample Preparation

For preparing commercial pellets for further characterizations and analysis, mechanical polishing, chemical etching and thermal etching were applied. Sample preparation has a significant role in getting expected results; for example for SEM images a flat surface is required where grains and grain boundaries are properly revealed. In the coming section the sample preparation required for different characterization techniques would be explained.

3.2.1.1 Polishing

All pellets (A to H) have been covered with conductive layers in both sides so mechanical polishing is required to remove them and make the surface smooth and flat. EDX results prove that the conductive layer is completely removed after mechanical polishing. Polishing machine BUEHLER, phoenix 4000 was applied to polishing the pellets. The first polishing paper was Grit400/P 800 which removed the conductive layers. Then Grit 600/P 1200, Grit 1000/P 2500 and silicon carbide 1200/4000 were used which resulted in a flat and shiny surface. After these 4 steps of polishing, the pellets were ready for SEM analysis, however characterization tools such as Electron Back Scattered Diffraction (EBSD) require even higher degree of flatness therefore diamond polishing cloth with colloidal silica suspension TED PELLA 0.06 µ were applied as an additional polishing step for these analysis.

3.2.1.2 Chemical etching

As explained in previous section, mechanical polishing was applied to making the top and bottom of pellets flat however etching was needed to be done for revealing the grains and grain boundaries. Therefore, two different chemical etchants were tested.
hydrochloric acid (HCL 32% concentration) and acetic acid (C₂H₄O₂ 99% concentration). HCl was tested for different etching times and temperatures and it was observed that due to over etching problems, the imaging quality remained poor. The second etchant (Acetic acid) was comparatively better than HCl, however identifying grain boundaries was still problematic.

3.2.1.3 Thermal etching

Since the chemical etching was not very successful, we tested using combination of mechanical polishing and thermal etching. The etching temperature was set to 1175 °C and two different heating rates (5 °C/min, 10 °C/min) were tested. We found the heating rate of 10 °C/min gives better results. All the SEM, EBSD analysis presented in this work uses the combination of mechanical polishing and thermal etching as described in these sections. The heating profile used for therm al etching is shown in Figure 3.1. At room temperature, as-polished pellets were placed in the furnace till the temperature got to 1175 °C/min so it took 117.5 minutes and then pellets were kept at this temperature for 2 hours then suddenly quenched in air.

This process was carried out in electrical tube furnace CARBOLITE type CTF/12/75/700 with 3000 W power and 50-60 Hz frequency which Figure 3.2 depicts.
it. It is believed that by thermal etching of the samples in air atmosphere, the oxidization process happens. This can be seen in section 3.2, Table 5.2.

3.2.2 Scanning Electron Microscopy (SEM)

The highest reachable magnification in the conventional optical microscope is around 1000x which is not sufficient for in-depth analysis of microstructural properties. Therefore, Scanning Electron Microscopy (SEM) with magnification up to 1,000,000x can be used for detailed microstructural analysis. The higher resolution of SEM compared to optical microscope is due to the lower wavelength of the electron beam used in this method compared to visible light’s wavelength. SEM can be used for collecting data about crystalline structure, surface topography and chemical composition. It should be mentioned SEM sample preparation is non-destructive and fast and easy [4]. Thus, this method is extensively used for studying the microstructure of materials.

Figure 3.2. Electrical tube furnace used for thermal etching process.
SEM is equipped with an electron gun on the top of the vacuum chamber. In this instrument, the sample is bombarded with and electron beam, then the electrons are either backscattered or secondary electrons are produced after the first collision due to interaction with sample. These two rays in addition to X-ray, cathode luminescence (not in our system), electron beam induced current and transmitted electrons are collected [73]. Figure 3.3 illustrates different processes that can happen when the electron beam interacts with the sample.

Hitachi SU-70 SEM with a field emission electron source fitted with a tungsten filament was applied in this research. Samples for SEM should be electrically conductive to prevent charging on the surface of insulator samples. Gold coating is usually exploited for solving this issue while it does not affect the compositional analysis. In order to stick the powder to sample holder, conductive carbon tape was
used. There is a chamber for specimen to enter and then 4 steps should be done for focusing, beam alignment, aperture alignment, stigma x and stigma y alignment. The accelerating voltage which was applied for powder was different in order to get a better quality and 3kV, 5kV, 10kV and 12kV were chosen.

3.2.3 Grain Size Distribution

In order to measure the grains size, SEM images were taken at 10-15 and 20 kV voltage and different magnification. Then grains sizes were measured by Image J software and their distribution was plotted using Origin software.

3.2.4 Energy Dispersive X-ray Spectroscopy (EDX)

Energy dispersive x-ray spectroscopy (EDX or EDS) is a technique used to determine the elemental composition of a sample. When the electron beam strikes the sample a number of different events occur such as secondary electrons, backscattered electrons and X-rays. The X-rays that are emitted when the beam encounters the sample are collected by the detector and used to analyse the samples composition. X-rays occur when an electron in a shell close to the nucleus absorbs the energy from the electron beam. The electron gains enough energy to overcome the binding energy barrier and be ejected from the shell. An electron from another orbital will then “fall” into the vacant position. When this electron drops into the inner shell a specific amount of energy is released in the form of electromagnetic radiation X-rays. This energy is specific to each element [74]. The electrons are generated and gathered by a lithium silicon detector, the detector is cooled with liquid nitrogen to reduce the electronic noise. The signal is generated and a spectrum is produced. To determine the composition the peaks in the spectrum are matched with peaks from standards. The electron beam with 20 kV energy was used for all EDX analysis in this research.
Image of selected area is transferred to INCA software. There are different ways to analyse the elements such as line scan, dot scan, area scan and mapping. Scan over area gives an overall scan from a low magnification image but others are more useful for higher magnification and special area or spots [74].

3.2.5 X-ray Diffraction Spectroscopy (XRD)

Discovery of x-rays dates back to 1895 when a German physicist Rontgen detected them for the first time. Nature of X-rays was unknown before 1912 and after that, their phenomenon were discovered. There are some similarities between ordinary light and x-rays such as effect on the photographic film and traveling in straight lines, however penetration depth of X-rays much larger. X-rays can penetrate in opaque material deeper and they are invisible unlike ordinary light[3].

Modern theory predicts dual nature of electromagnetic radiation, i.e. they exhibit both particles and waves properties simultaneously. This is unlike the classical theory, which treats electromagnetic radiations strictly as waves and in quantum theory they are considered as a stream of particles called photons [3].

X-ray is produced when the material is bombarded with accelerated electron beam. This energy excites the electrons to higher energy levels [75]. The excited electrons tend to come back to their basic energy level. The excess energy released in this process is called X-ray.

X-ray is used in studying the crystal structure of materials. For this purpose, X-ray is radiated to the samples. Diffraction occurs when an x-ray beam strikes a structure and the wavelength of the x-ray beam is similar to the spacing of the atoms in the structure. When an x-ray beam strikes a 3-D arrangement of atoms in a structure most of the x-rays will destructively interfere with each other and cancel each other out. But in some specific
directions the x-rays will constructively interfere and reinforce one another. It is these reinforced or diffracted x-rays that produce the distinctive diffraction patterns that are used for sample identification. Based on the Bragg’s law [76] if the path length difference of 2 incident beam equals an integer value of their wavelength then diffraction will happen:

\[ AB = BC = \text{path length difference} \]

Where, \( n \) is an integer (1, 2, 3...), \( \lambda \) is the wavelength, \( d \) is the distance between the atomic planes [3].

Figure 3.4 shows a simple schematic of x-ray diffraction.

![Figure 3.4. Schematic of x-ray diffraction by a crystal [3]](image)

The PANalytical X’Pert PRO MPD X-ray diffractometer with reflection geometry was used to perform structural analysis of the commercial pellets. First conductive layers of pellets were removed by polishing then samples were loaded to XRD machine. Monochromated Cu K\( \alpha \) ray was used with 40 kV and 35 mA. The scan was done in the range of 10\(^\circ\) and 80\(^\circ\).
3.2.5.1 Non-Ambient Temperature XRD

For high temperature XRD analysis, the PANalytical X’Pert PRO MPD X-ray machine was employed. This analysis was performed to study the variation in the crystal structure with temperature. This setup consists of a small furnace which is connected to the diffractometer and can keep the sample at the desired temperature during the XRD pattern collection.

![Non-Ambient Temperature XRD setup.](image)

In this research, high temperature XRD patterns of industrial samples D and the samples which was SPS sintered at 1000 °C for 3 minutes with 50 °C/min heating rate were collected at 25 °C, 100 °C, 200 °C and 300 °C. This was done to compare the phase transition in the best performing industrial samples (Sample D) and the in house SPS sintered doped barium titanate sample.

3.2.6 Raman Spectroscopy

Discovery of Raman spectroscopy dates back to 1928 when an Indian physicist found light can have inelastic scattering which is known as Raman Effect nowadays. Inelastic
scattering means that the frequency of photons changes upon interaction with sample. In this phenomenon, when monochromatic light is radiated on a sample, it may interact with sample in some ways. It may reflected, absorbed or scattered. The scattering of light is the part which can reveal some information about the sample. The frequency of the scattered light is shifted up or down compared to the original monochromatic frequency. The incident of light with molecules, create and induced electric dipole moment which deforms molecule. In other words, the monochromatic light with frequency $\nu_0$, transforms molecules into oscillating dipoles. These dipole emit light in three different frequencies:

(a) A molecule with no Raman active mode absorbs the phonon with frequency $\nu_0$, gets excited and then returns back to the basic vibrational state. A light with the same frequency is emitted. This is called and elastic Rayleigh scattering.

(b) A Raman active molecule which is in basic vibrational state, absorbs the light with frequency $\nu_0$. Part of it is converted to Raman active mode with frequency $\nu_m$. Thus the final frequency of the scattered light is $\nu_0 - \nu_m$. This is called a Stokes frequency.

(c) The light is absorbed by a Raman active molecule which is already at excited state. When molecule return back to the basic state, the excessive energy is released $\nu_m$. Then the frequency of the scattered light goes up to $\nu_0 + \nu_m$. This is called Anti-Stokes frequency.

Raman technique uses scattered light to obtain information about molecular vibration that it can be really helpful to collect information about molecule bonding, symmetry and structure. With Raman analysis both quantitative and qualitative information can be accessed. So the vibrational spectrum which is gained by Raman techniques is
applied as a fingerprint ID for structures and makes their interpretation easier and more reachable[77].

A simple schematic of components in Raman spectrometer is shown in Figure 3.6.

Raman spectroscopy was carried out on Horiba Jobin Yvon LabRAM using laser with wavelength 532 nm, filter 100% and grating 1800.

### 3.2.7 Electron Back Scattered Diffraction Spectroscopy (EBSD)

Electron Back Scattered Diffraction is a kind of SEM based technique. The basic operation of this method is forming a pattern on a phosphor screen in SEM chamber by diffracted backscattered electrons. This diffracted pattern is able to gain valuable information such as grain size, pole figure and orientation mapping. The technique has improved significantly in terms of speed in the last ten years and nowadays it has wide range application in the industry. Normal acquisition time for recent EBSD detector is one hour for 100×100 µm² area. In this method for producing more backscattered
electron, accelerating voltage should not be less than 15 kV and sample surface smoothness is really important to get a good results [66]. Figure 3.7 shows a simple schematic of operation in EBSD test. As it can be seen sample should be highly tilted between 60° to 80° towards the detector in order to enhance the quality of pattern which will be achieved.

![Figure 3.7. Schematic representation of EBSD apparatus.](image)

In current research in order to prepare samples for EBSD, after thermal etching of as-polished industrial pellets, some extra polishing is needed to gain a really smooth and flat surface so diamond cloth was applied for the final step of polishing and colloidal silica made this process quicker and more efficient. Gold coating was applied to prevent charging and drifting during the scan as the samples are not conductive. The same procedure for gold coating was employed as mentioned previously for powders.
The gold coating fills the cracks and voids in the sample with a conducting network which prevent charging.

After transferring the diffraction pattern from camera to the EBSD software, the Hough transform is used to calculate the position of the Kikuchi bands. By identifying the Kikuchi bands position, the angles between the detected bands can be calculated. Then the calculated angles are compared with a list of interplanar angles of the analysed structure and the possible solutions are sorted to find the best fit. In the Hough transform, the following equation is used to transform coordinates \((x,y)\) to coordinates \((\rho,\theta)\) of the Hough space:

\[
\rho = x\cos\theta + y\sin\theta
\]

(3.1)

3.2.8 Atomic Absorption Spectroscopy (AAS)

Atomic Absorption Spectroscopy is one of the useful techniques to identify the quantity of elements in materials. Atomic absorption has two methods: Flame AAS and furnace AAS. If the analysed concentration in solution is more than mg/lit range, flame AAS is the most precise analytical methods to find the concentration of elements in the samples which can be prepared as a solution. AAS has a time-consuming sample and standard preparation procedure process. Compared to EDS analysis, this method has higher sensitivity which is around less than 1% error in the final results [78]. In this research, the target was finding the composition of the best performing commercial sample (so-called pellet D). All AAS tests in this research were done in Varian/Spectra AA 220 instruments. The obtained chemical composition of sample D was used as benchmark for preparation of synthesized powders. Powder synthesis process will be explained in section 3.3. The sample preparation for AAS involves
digestion of ceramic pellets in Anton Par microwave digester Multiwave PRO. For this pellet D was ground in the milling machine, then 25 mg of powders were weighed and 30 ml HCl 37% was applied as a solvent. The digester was set on 90 minutes for power hold, 30 minutes for cooling and 15 minutes for power ramp. In order to assure about the homogeneity of the sample D, three different batches were used to make original solutions. Also, standard solutions of each element (Ba, Ti, Sr, Pb and Ca) were prepared according to the optimum working range mentioned in flame atomic absorption spectroscopy analytical methods reference. Standard solutions with various concentration are represented in Table 3.1.

<table>
<thead>
<tr>
<th>Elements</th>
<th>Standard Concentrations (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ba</td>
<td>1</td>
</tr>
<tr>
<td>Ca</td>
<td>0.2</td>
</tr>
<tr>
<td>Sr</td>
<td>0.5</td>
</tr>
<tr>
<td>Ti</td>
<td>1</td>
</tr>
<tr>
<td>Pb</td>
<td>1</td>
</tr>
</tbody>
</table>

3.3 Powder Synthesis

3.3.1 Powder Preparation -Mixing and Milling

The first step in sample preparation is the right choice of precursors, which is dependent upon the synthesis route being adopted. We chose the ratio of the precursors in such a way that it matches sample D chemistry which is the bench mark sample in this study. In this regard we employ the results of EDX analysis on sample D and use them as a guideline to select adequate ratio of the precursors. Solid State Synthesis
(SSS) procedure was employed to process powders; the details of SSS procedure will be explained in the coming sections. The precursors were carefully weighed on a digital balance according to pre-determined ratios of different elements in sample D, they were blended in a 500 ml polyethylene bottle with Ethanol as a solvent and zirconia milling balls (1.5 mm diameter). The ratio of milling balls to powders was kept 1:10 for all samples in this study. The polyethylene bottle containing the mixture of milling balls and powders is placed in the milling machine (Tumbler) for 8 hours milling. The Tumbler used for the sample preparation is shown Figure 3.8.

![Figure 3.8: Planetary milling machine](image)

### 3.3.2 Solid State Synthesis Route

In this method as described in section 3.3.2, precursors were BaCO$_3$ (99.9%-Ba, Sr < .03%), TiO$_2$ (+99%), SrCO$_3$ (97%), CaCO$_3$ (98%) all from STREM CHEMICALS INC. and PbCO$_3$ from ACROS ORGANICS. The first step is mixing and milling. In order to extract CO$_2$ gases, powders should be calcined. Precursors were mixed together with different ratios according to Table 3.2. The processed powders are then analysed with AAS to determine the precise amount of elements, The AAS analysis
shows that SSS-4 is the most matched composition with sample D; we chose this combination for further processes and experiments.

Table 3.2. Weight% of precursors used in Solid State Synthesis route

<table>
<thead>
<tr>
<th>Methods</th>
<th>BaCO\textsubscript{3} (Wt %)</th>
<th>TiO\textsubscript{2} (Wt %)</th>
<th>SrCO\textsubscript{3} (Wt %)</th>
<th>PbCO\textsubscript{3} (Wt %)</th>
<th>CaCO\textsubscript{3} (Wt %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SSS-1</td>
<td>51.9</td>
<td>27.4</td>
<td>1</td>
<td>16.2</td>
<td>3.2</td>
</tr>
<tr>
<td>SSS-2</td>
<td>36.5</td>
<td>22.8</td>
<td>1.8</td>
<td>31.9</td>
<td>6.8</td>
</tr>
<tr>
<td>SSS-3</td>
<td>38.1</td>
<td>23.8</td>
<td>1.9</td>
<td>33.3</td>
<td>2.8</td>
</tr>
<tr>
<td>SSS-4</td>
<td>47.6</td>
<td>28.3</td>
<td>1.3</td>
<td>19.2</td>
<td>3.4</td>
</tr>
</tbody>
</table>

Figure 3.9. Schematic diagram for milling process of Solid State Synthesis route
3.3.3 Calcination

In Solid State Synthesis route when milling process was finished in order to have \( \text{BaTiO}_3 \), powders should be calcined in purpose of removing \( \text{CO}_2 \) gases [79]. In this process, all the carbonates convert to \( \text{CO}_2 \) and the correspondent oxides (\( i.e. \) \( \text{BaO}, \text{SrO}, \text{PbO} \) and \( \text{CaO} \)). This process was done in LENTON electrical box furnace for 4 hours at 1100\(^\circ\)C. After calcination powders were milled again for 8 hours, dried and sieved with 425 microns (mesh 40) and 125 microns (mesh 120).

3.4 Spark Plasma Sintering

In order to study the effect of different sintering parameters on structural and microstructutal properties of barium titanate doped samples, prepared powders were sintered into discs of 10mm diameter and approximately 2 mm thickness. Applied pressure of 90 MPa were used for all samples (7KN force on the 10mm diameter die). Effect of three different parameters on morphology, grain size, composition, crystal structure and density were studied such as heating rate, sintering temperature and soaking time. The design of experiment (DOE) for current research has been illustrated in Table 3.3.
Table 3.3. Design of experiment for sintering of BaTiO$_3$

<table>
<thead>
<tr>
<th>Heating rate (°C/min)</th>
<th>Sintering temperature (°C)</th>
<th>Soaking time (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Experiment set 1 (Different heating rates)</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>50</td>
<td>1000</td>
<td>3</td>
</tr>
<tr>
<td>100</td>
<td>1000</td>
<td>3</td>
</tr>
<tr>
<td>150</td>
<td>1000</td>
<td>3</td>
</tr>
<tr>
<td>200</td>
<td>1000</td>
<td>3</td>
</tr>
<tr>
<td><strong>Experiment set 2 (Different sintering temperatures)</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>50</td>
<td>800</td>
<td>3</td>
</tr>
<tr>
<td>50</td>
<td>850</td>
<td>3</td>
</tr>
<tr>
<td>50</td>
<td>900</td>
<td>3</td>
</tr>
<tr>
<td>50</td>
<td>950</td>
<td>3</td>
</tr>
<tr>
<td><strong>Experiment set 3 (Different soaking times)</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>50</td>
<td>1000</td>
<td>3</td>
</tr>
<tr>
<td>50</td>
<td>1000</td>
<td>5</td>
</tr>
<tr>
<td>50</td>
<td>1000</td>
<td>7</td>
</tr>
<tr>
<td>50</td>
<td>1000</td>
<td>10</td>
</tr>
</tbody>
</table>

The 1000 °C was chosen as a start point because it has been revealed that at higher temperatures no significant change in density were observed while exaggerated grain growth was increased [10]. The lower temperatures were also investigated to elucidate the effect of sintering temperature on this specific case. Also, different heating rates from 50 °C/min to 200 °C/min were chosen in order to clarify its effect on microstructural properties of the samples. Soaking time was the last parameter to be studied. As SPS method is an effective and fast method, short soaking times from 3 to 10 minutes were selected.
3.4.1 Characterisation

In order to study structure, microstructure, morphology and chemical composition of sintered specimens, different characterization techniques such as SEM, EDX, XRD and density measurements were applied. The characterisation methods were used based on the procedure mentioned in sections 3.2.2, 3.2.4 and 3.2.5, respectively. Steps for sample preparation before characterization was done exactly as the same as procedures mentioned in section 3.2.1.1 and 3.2.1.3 for polishing and thermal etching.

3.4.1.1 Density measurements

The density of the as-sintered samples was measured using Archimedes method for 3 samples of each batch. Figure 3.10 shows the setup for this method. For density measurements, the dry and wet weight of the sample were measured. The wet weight was measured while the samples were immersed in deionized water. The density was calculated based on the equation (3.2).

\[
\rho_s = \rho_{fl} \frac{m(s)}{m(fl)}
\]  

(3.2)

Where, \( \rho_s \) and \( \rho_{fl} \) are the density of the samples and liquid, respectively. \( m_s \) and \( m_{fl} \) are the mass of specimen and the fluid inside the beaker. In this equation it is required that the mass of the displaced water is known since this is directly related to the volume of the sample. As the mass of displaced water cannot be easily identified, the density can be measured based on the wet and dry mass of the object. As a result, the following equation can be used for indicating the density of the samples without knowing the volume of the object (mass of the displaced water).
\[ \rho_s = \rho_f \frac{m_d}{m_d - m_w} \]  

(3.3)

Where, \( m_d \) is the weight of the sample when it is dry, \( m_w \) is the weight of the object after it is completely immersed in water. Based on this equation, the density of the samples can be calculated without knowing the exact volume of the samples.

3.4.1.2 Resistivity Measurements

The resistivity of the industrial and sintered samples was measured by using a simple circuit showed in Figure 3.10. This setup is consisted of the sample which is already sputtered with a conductive layer (here Ni/Al) to provide conductive contacts. The sample is then inserted between two conductive electrodes which are connected to the power supply. The ammeter is put in the circuit in series with the samples while the voltmeter is in parallel to measure the current and voltage of the sample.

![Figure 3.10. Experimental setup for density measurement.](image)
A thermocouple is also in a solid contact with the sample in order to measure the change in the temperature during the resistivity measurement. Finally, the variations of resistivity versus temperature were measured by using 10 V of electrical potential to the sample. The resistivity is measured as a function of using the simple Ohm’s law equation (3.4)

\[ R = \frac{V}{I} \]  \hspace{1cm} (3.4)

Where, \( R \) is the resistivity, \( V \) is the applied voltage to the sample, and \( I \) is the electrical current passing through the sample.
Chapter 4  : Structural Characterisation of Commercial PTC Stones

4.1 Introduction

Commercial PTC stones labelled A - H were supplied by industrial partner BorgWarner Tralee. All obtained samples were characterized to extract data on morphology using scanning electron microscope, grain size distribution, compare the chemical composition by Energy Dispersive X-ray Spectroscopy and measure thickness of the conductive layers. Crystal structures were studied by XRD analysis and chemical compositions were characterized by Raman Spectroscopy. Finally, EBSD patterns were employed to study preferential orientation in grains. Also, AAS test were employed to find the accurate elemental composition and dopants in pellet D. The purpose of all those characterizations for commercial samples is trying to match performance in currently available PTC thermistors.

4.2 Morphology of PTC stones by Scanning Electron Microscopy (SEM)

SEM images of tested samples are presented in Figure 4.1, as it can be seen in the images shape and size of grains for all samples A to G more or less are the same and they are densified but sample H obviously has different microstructure. Grains are more spherical in sample H and they have smaller size in comparison to the others. All images were taken with voltage 15 kV and magnification 3000X. The average grain size for all pellets has been measured and reported in next section.
4.3 Grain Size Distribution

In order to compare distribution of grain sizes in samples, microscope images were analysed. In Figure 4.2 bar charts of grain size distribution are presented. All bar charts have normal distribution. In Table 4.1 the mean value or average grain size of each PTC pellets are listed. The finest average grain diameter is in Pellet H (2.9 micrometres) while the biggest average grains diameter is 4.4 micrometres in pellet
D. Distribution curve for sample H is narrower. The range of grain sizes is narrow and microstructure is more homogeneous compared to other samples. The range of grain size for pellet A to G is approximately between 1 μm to 9 μm while pellet H has the narrower range from 1 μm to 6 μm.
Figure 4.2. Grain size distribution for all thermally etched pellets

Table 4.1. Average grain size for all PTC pellets

<table>
<thead>
<tr>
<th>Pellet</th>
<th>Average grain size (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>3.88</td>
</tr>
<tr>
<td>B</td>
<td>4.23</td>
</tr>
<tr>
<td>C</td>
<td>3.36</td>
</tr>
<tr>
<td>D</td>
<td>4.48</td>
</tr>
<tr>
<td>E</td>
<td>3.77</td>
</tr>
<tr>
<td>F</td>
<td>4.01</td>
</tr>
<tr>
<td>G</td>
<td>3.69</td>
</tr>
<tr>
<td>H</td>
<td>2.97</td>
</tr>
</tbody>
</table>
4.4 Energy Dispersive X-ray Spectroscopy (EDX)

In current research, EDX was done on different grains and areas of the samples. The analysis was employed to find the possible elements and weight percent of each element in conductive layer and bulk of the pellets. To study the composition of bulks, conductive layers were removed by polishing. Afterward, thermal etching (heat treatment) was carried out to reveal the grains and grain boundaries. This method were applied for two types of measurements: “area identification analyses” in low magnification to get composition for bigger area and “point identification analyses” in high magnification for checking segregation of elements at specific point of analysis. EDX analysis results are presents in following sections.

4.4.1 EDX results for bulk of as-received PTC stones

In order to study the chemistry in bulk of the samples, combination of cross section SEM imaging technique and EDX analysis were employed. Following elements were found in the bulk of PTC pellets: Barium (Ba), Titanium (Ti), Strontium (Sr), Calcium (Ca) and Lead (Pb). EDX test was done on all 8 pellets in high and low magnification. High magnifications were used for dot scans while low magnifications were applied for area scans. In dot scan, 6 spectrums were chosen and the mean values for all of them are presented in Table 4.2. Samples A to G have similar composition and sample H showed different elemental composition. According to EDX results, Pb and Sr in sample H are low or close to zero and this sample mostly contains Ba and Ti.
Table 4.2. EDX analysis result for bulk of cross sectional part of as-received pellets (in high and low magnification)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Magnification</th>
<th>Ca(Wt%)</th>
<th>Ti(Wt%)</th>
<th>Sr(Wt%)</th>
<th>Ba(Wt%)</th>
<th>Pb(Wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>High</td>
<td>2.14</td>
<td>26.43</td>
<td>1.31</td>
<td>54.18</td>
<td>15.94</td>
</tr>
<tr>
<td></td>
<td>Low</td>
<td>2.03</td>
<td>25.69</td>
<td>0.82</td>
<td>54.58</td>
<td>16.88</td>
</tr>
<tr>
<td>B</td>
<td>High</td>
<td>1.83</td>
<td>25.41</td>
<td>1.05</td>
<td>54.68</td>
<td>17.02</td>
</tr>
<tr>
<td></td>
<td>Low</td>
<td>1.95</td>
<td>25.86</td>
<td>0.94</td>
<td>54.24</td>
<td>17.02</td>
</tr>
<tr>
<td>C</td>
<td>High</td>
<td>1.65</td>
<td>24.12</td>
<td>0.82</td>
<td>57.36</td>
<td>16.05</td>
</tr>
<tr>
<td></td>
<td>Low</td>
<td>1.84</td>
<td>24.92</td>
<td>0.65</td>
<td>56.48</td>
<td>16.11</td>
</tr>
<tr>
<td>D</td>
<td>High</td>
<td>1.88</td>
<td>25.58</td>
<td>1.04</td>
<td>57.67</td>
<td>13.83</td>
</tr>
<tr>
<td></td>
<td>Low</td>
<td>1.77</td>
<td>23.83</td>
<td>0.29</td>
<td>56.61</td>
<td>17.51</td>
</tr>
<tr>
<td>E</td>
<td>High</td>
<td>2.33</td>
<td>25.70</td>
<td>1.53</td>
<td>53.47</td>
<td>16.97</td>
</tr>
<tr>
<td></td>
<td>Low</td>
<td>1.86</td>
<td>24.88</td>
<td>0.96</td>
<td>54.68</td>
<td>17.62</td>
</tr>
<tr>
<td>F</td>
<td>High</td>
<td>1.87</td>
<td>25.78</td>
<td>1.19</td>
<td>56.28</td>
<td>14.87</td>
</tr>
<tr>
<td></td>
<td>Low</td>
<td>1.89</td>
<td>25.09</td>
<td>0.93</td>
<td>55.00</td>
<td>17.09</td>
</tr>
<tr>
<td>G</td>
<td>High</td>
<td>2.01</td>
<td>25.44</td>
<td>1.12</td>
<td>53.32</td>
<td>18.10</td>
</tr>
<tr>
<td></td>
<td>Low</td>
<td>2.07</td>
<td>25.85</td>
<td>1.15</td>
<td>53.56</td>
<td>17.36</td>
</tr>
<tr>
<td>H</td>
<td>High</td>
<td>0.31</td>
<td>29.61</td>
<td>0</td>
<td>70.08</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>Low</td>
<td>0.60</td>
<td>29.32</td>
<td>0</td>
<td>70.09</td>
<td>0</td>
</tr>
</tbody>
</table>

Figure 4.3 shows the 6 points which were selected for point identification analysis in high magnification. The chemical composition of the other samples are tabulated in Table 4.3 based on the average values of EDX point analysis.

![Figure 4.3](image)

Figure 4.3. Point identification analyses in cross-sectional part of bulk in as-received sample C
Comparison of composition of the bulk as-received samples (with conductive layer) is presented in Figure 4.4. The chemical composition of samples A to G is in the same range. In all the samples 5 main elements are recognized in the following order: Ba (55 wt%), Ti (25 wt%), Pb (15 wt%), Ca (2.5 wt%) and Sr (2 wt%). However, pellet H has different concentration of mentioned elements: concentrations of Ba and Ti are around 70 wt% and 30 wt%, respectively. However, no additives (Pb, Sr, and Ca) were detected in the chemical composition of this sample.

Figure 4.4. Average concentration of Ca, Ti, Sr, Ba and Pb for bulk of as-received pellets cross-section in high magnification by EDX analysis
Figure 4.5 shows the selected area for low magnification EDX analysis of cross-sectional part of the bulk in as-received sample C as an example.

![Image](image.png)

**Figure 4.5.** Area scan in low magnification EDX analysis for cross-sectional part of bulk in as-received sample C

The related concentration of Ca, Ti, Sr, Ba and Pb in cross-sectional part of bulk of original samples in low magnification are illustrated in Figure 4.7 below. Results of low magnification EDX analysis are as the same as for high magnification analysis as expected.
4.4.2 EDX results for surface of thermally etched pellets

In this section, the results of EDX done on the thermally etched surface of PTC pellets are presented. Dot scans were carried out in high magnification. As presented in Figure 4.8 results of each element for sample A to G are in the same range but sample H has lower amount of Pb, Ca and Sr. Also, it has higher values of Ba and Ti compared to other characterised samples.

Figure 4.8 and Figure 4.9 illustrate the whole range of chemical composition of all samples in high magnification and low magnification respectively. Weight percentage of Ba, Ti and all dopants (Sr, Ca and Pb) for samples A to G are in the same range. Moreover, results in high and low magnification are quite similar.
Table 4.3. EDX analysis results on the surface of thermally etched pellets (high and low magnification)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Magnification</th>
<th>Proportional composition of samples</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Ca(Wt%)</td>
</tr>
<tr>
<td>A</td>
<td>High</td>
<td>2.23</td>
</tr>
<tr>
<td></td>
<td>Low</td>
<td>1.85</td>
</tr>
<tr>
<td>B</td>
<td>High</td>
<td>2.25</td>
</tr>
<tr>
<td></td>
<td>Low</td>
<td>2.06</td>
</tr>
<tr>
<td>C</td>
<td>High</td>
<td>2.23</td>
</tr>
<tr>
<td></td>
<td>Low</td>
<td>2.06</td>
</tr>
<tr>
<td>D</td>
<td>High</td>
<td>2.29</td>
</tr>
<tr>
<td></td>
<td>Low</td>
<td>2.17</td>
</tr>
<tr>
<td>E</td>
<td>High</td>
<td>2.36</td>
</tr>
<tr>
<td></td>
<td>Low</td>
<td>1.70</td>
</tr>
<tr>
<td>F</td>
<td>High</td>
<td>2.27</td>
</tr>
<tr>
<td></td>
<td>Low</td>
<td>1.53</td>
</tr>
<tr>
<td>G</td>
<td>High</td>
<td>2.35</td>
</tr>
<tr>
<td></td>
<td>Low</td>
<td>2.12</td>
</tr>
<tr>
<td>H</td>
<td>High</td>
<td>0.27</td>
</tr>
<tr>
<td></td>
<td>Low</td>
<td>0.53</td>
</tr>
</tbody>
</table>
4.4.3 EDX results for bulk and conductive layer in commercial PTC stones

EDX analysis was performed on both bulk and conductive layers of the samples in order to find the difference in their chemical compositions. For all samples point analysis was done on conductive layer and bulk. Spectrums 1 and 2 are chosen in conductive layer and the rest (spec 3, 4, 5 and 6) are in bulk (Figure 4.10).
Figure 4.9. EDX results for thermally etched surface of pellets A to H at low magnifications.

4.4.3.1 Sample A:

The chosen spectra in conductive layer and bulk of original sample A in cross-section SEM image can be seen in Figure 4.10. Spectra 1 and 2 were selected in the conductive layer and the rest of them were chosen in bulk area to make a comparison between the chemical compositions of these two regions. This trend has been followed for all other industrial samples. The results revealed that the chemical composition of the conductive layer and the bulk of the pellets are completely different.

Specifically, conductive layer of sample A contains high amounts of aluminium. This can be related to the presence of an aluminium conductive layer of these samples. However, negligible amounts of aluminium were measured in the bulk of the sample A. The EDX analysis of the bulk of sample A shows the presence of Ca, Sr, Ba, Ti
and Pb as main elements. This trend for both conductive layers and bulk was also seen in samples B to G. Sample H had the lowest amount of Pb (almost zero) based on the bulk EDX analysis results. (Appendix A: Chapter 4)

**Figure 4.10.** Cross-sectional image of original pellet A with conductive layer used for EDX analysis

![Cross-sectional image of original pellet A with conductive layer](image)

**Figure 4.11.** (a) EDX results in pie chart for conductive layer of original sample A (b) EDX results for bulk of original sample A.

### 4.5 Thickness measurements for conductive layer of PTC stones

The thickness of the conductive layer was measured from SEM images. To distinguish the bulk from conductive layer EDS dot scans were done. As it is depicted in
Figure 4.11 there is a difference between the microstructure of conductive layer and the substrate in all samples. This can be related to the different compositions as stated in previous sections. Also, the thickness of the layers have been measured and the values for samples A to G are between 14 to 24 µm. However, in sample H as it is depicted it is 48.8 µm.

Figure 4.11. Cross sectional SEM images of conductive layer and substrate of original samples A to H.
Also, the thickness of the top layer is almost in the same range for all samples except samples H.

As it can be seen, the thickness of the conductive layer in all samples was in the range of 14.3 µm to 24.73 µm, while this is not the case in sample H. The thickness of conductive layer in sample H is around 48.8 µm which is thicker than all the other industrial samples. The thickness of conductive layer in samples from Supplier 1 is 20±5 µm.

4.6 X-ray Diffraction analysis (XRD)

X-ray diffraction analysis was carried out on all industrial samples to investigate their crystal structure and phase composition. The XRD spectra are presented in Figure 4.13. All samples are crystallized in tetragonal crystal structure at room temperature. This is concluded based on the doublet peak at 45° which is correspondent to hkl Miller index (002) and (200). These two planes are specific
characteristics of tetragonal barium titanate[80]. The crystallographic planes of sample A are mentioned in Error! Reference source not found.. These planes were also detected in other samples. HighScore software was used to search and match the XRD patterns of the samples with potential candidates. The first determined candidate is Ba$_{0.8}$O$_3$Pb$_{0.2}$Ti$_1$ Barium Lead Titanium Oxide with ICSD file ref.no. 98-007-9217. Second matched candidate is Ba$_{0.88}$Ca$_{0.12}$O$_3$Ti$_1$ Barium Calcium Titanate with ICSD file ref.no. 98-003-0045 and the third candidate is Ba$_{0.67}$O$_3$Sr$_{0.33}$Ti$_1$ Barium Strontium Titanate with ICSD file ref.no. 98-002-4419.
Figure 4.13. XRD pattern of industrial samples A to H.
Figure 4.15. The crystallographic planes of the samples A to H based on the XRD patterns.
Figure 4.14 shows which peaks from $\text{Ba}_{0.8}\text{O}_{3}\text{Pb}_{0.2}\text{Ti}_{1}$ composition with the industrial sample A.

Figure 4.15 and Figure 4.16 depict the matched spectrum of $\text{Ba}_{0.88}\text{Ca}_{0.12}\text{O}_{2.79}\text{Ti}_{0.93}$ and $\text{Ba}_{0.67}\text{O}_{3}\text{Sr}_{0.33}\text{Ti}_{1}$ with the industrial sample A. Furthermore, Figure 4.16 illustrates the matched peaks of the industrial sample and $\text{Ba}_{0.67}\text{O}_{3}\text{Sr}_{0.33}\text{Ti}_{1}$. The same three mentioned phases were also detected to be present in samples B to H.
Figure 4.15. Matched peaks of sample A with Ba$_{0.67}$Ca$_{0.33}$Ti$_{1}$ reference peaks.

Figure 4.16. Matched peaks of sample A with Ba$_{0.88}$Ca$_{0.12}$O$_{2.79}$Ti$_{0.93}$ reference peaks.
4.7 Raman Spectroscopy

4.7.1 Raman spectra for polished PTC stones

Raman spectra of samples A to H at room temperature are presented in Figure 4.17. It is good to remember that barium titanate is in tetragonal crystal structure at room temperature. All active modes of tetragonal crystal structure were observed [81, 82].

![Raman spectra of polished samples (without conductive layer).](image)

**Figure 4.17.** Raman spectra of polished samples (without conductive layer).

4.7.2 Raman spectra for thermally etched PTC pellets

The Raman spectra of thermally etched samples at room temperature show the tetragonality of the samples A to H [82]. Also, no difference between the Raman spectra of thermally etched and polished samples were observed.
After the comprehensive examination of the chemical composition via XRD and Raman spectroscopy, the ferroelectricity and the preferential orientation of the grains were studied via electron back scattered diffraction (EBSD) techniques. The results are discussed in section 4.8.

4.8 Electron Back Scattered Diffraction Spectroscopy (EBSD)

4.8.1 EBSD pattern of pellet A

To study the grain orientations in the industrial samples, EBSD technique was employed. Samples were prepared as described in section 3.2.7. Thermal etching was performed prior to EBSD to reveal the grain boundaries. In Figure 4.19 a high resolution SEM image of industrial sample A after thermal etching is depicted. Figure 4.19A shows the 2000x SEM image of the polished surface. The grains and
grains boundaries in addition to ferroelectric domains can be seen clearly based on the contrast. (Red arrows on SEM image) Figures 4.20 B and C illustrate the selected area for EBSD analysis. The surface is flat enough for EBSD analysis.

Figure 4.19. (A) High resolution SEM image of studied sample, (B) the selected area for EBSD analysis, (C) the band contrast of the selected area.

Figure 4.20 shows EBSD patterns, pole figure maps and SEM images of the industrial thermally etched samples A. Ferroelectric domains can be seen in SEM images while observed domains on SEM images do not have the same direction however, local grain orientations were noticed in EBSD patterns. As different colours represent different
crystal orientation (see legend) BaTiO$_3$ grains have distinctive orientation, but locally a preferential orientation was also noted. Since no external electrical field was applied to tested samples - they are weakly polarised. Furthermore, pole figure map density is an indicator of preferential orientation and if the maximum value is above 20 it can be claimed that the grains have preferential orientation. In obtained pole figure maps, maximum density is within 6.5 – 8.5 range, so based on above studies no preferential orientation can be marked.

![Figure 4.20. EBSD pattern of thermally etched industrial sample A.](image)

### 4.10 Resistivity measurements

Resistivity measurements were performed on 3-5 specimens of each batch of industrial samples. This was done in order to check the homogeneity in electrical properties of the samples. Among all other specimens, sample D showed the most consistent PTC
performance. The lowest deviation of the resistivity-temperature measurements were observed in sample D. This is due to the higher homogeneity in chemical composition, and sintering procedure for sample D. However, other samples showed higher deviations. Based on this results, sample D was chosen as a benchmark for further studies.

In Figure 4.21 resistivity versus temperature is plotted for samples A to H. An increase in resistivity at higher temperatures was revealed in all samples which is related to the PTC effect of barium titanate.

![Resistivity measurements versus temperature for all industrial samples.](image)

**Figure 4.21.** Resistivity measurements versus temperature for all industrial samples.
Chapter 5  : Spark Plasma Sintering of BaTiO$_3$

5.1 Introduction

The aim of this chapter is to study the effect of spark plasma sintering parameters on microstructure of BaTiO$_3$. Following parameters were analysed: heating rate, temperature of sintering and soaking time. Samples were sintered from powders prepared with chemical composition of sample D following the mentioned procedure in section 3.3. Four different heating rate (50°C/min, 100°C/min, 150°C/min and 200°C/min) were chosen. Study of different sintering temperature was done by testing five various temperatures (800°C, 850°C, 900°C, 950°C and 1000°C). Finally, to investigate the effect of soaking time, four different soaking times (3 minutes, 5 minutes, 7 minutes and 10 minutes) were examined at optimised sintering temperature. Details of the DoE are presented in Table 5.1.

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Heating Rates</th>
<th>Sintering Temperature</th>
<th>Soaking Time</th>
</tr>
</thead>
<tbody>
<tr>
<td>Step 1</td>
<td>50 °C/min</td>
<td>1000 °C</td>
<td>3 minutes</td>
</tr>
<tr>
<td></td>
<td>100 °C/min</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>150 °C/min</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>200 °C/min</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Step 2</td>
<td>50 °C/min</td>
<td>800 °C</td>
<td>3 minutes</td>
</tr>
<tr>
<td></td>
<td></td>
<td>850 °C</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>900 °C</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>950 °C</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>1000 °C</td>
<td></td>
</tr>
<tr>
<td>Step 3</td>
<td>50 °C/min</td>
<td>1000 °C</td>
<td>3 minutes</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>5 minutes</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>7 minutes</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>10 minutes</td>
</tr>
</tbody>
</table>
5.2 Study the effect of different heating rates

In step 1, the main aim was to study the effect of different heating rates on the microstructure of the samples. For this purpose, samples were sintered at 1000 °C for 3 minutes under 90 MPa at various heating rates (50, 100, 150 and 200 °C/min). As mentioned in the literature, at temperatures higher than 1000 °C no big difference in density was seen, while an exaggerated grain growth was happened. As a result, 1000 °C was chosen as the starting point. In Table 5.2 shape and colour of sintered samples are presented before and after thermal etching. Spark Plasma Sintered samples before thermal etching are dark grey while after heat treatment in air at 1175 °C their colour changed to bright beige. The change in colour might be referred to oxidation process during thermal etching.

<table>
<thead>
<tr>
<th>Sintering conditions: Sintering temperature: 1000 °C Soaking time: 3 minutes</th>
<th>Before Thermal Etching</th>
<th>After Thermal Etching</th>
</tr>
</thead>
<tbody>
<tr>
<td>Heating rate 50 °C/min</td>
<td><img src="image1.png" alt="Image" /></td>
<td><img src="image2.png" alt="Image" /></td>
</tr>
<tr>
<td>Heating rate 100 °C/min</td>
<td><img src="image3.png" alt="Image" /></td>
<td><img src="image4.png" alt="Image" /></td>
</tr>
</tbody>
</table>
5.2.1 Morphology and microstructure

Figure 5.1 shows the SEM images of samples sintered at 50 °C/min, 100 °C/min, 150 °C/min and 200 °C/min heat rate and spark plasma sintered at 1000°C for 3 minutes, respectively. To reveal grains and grain boundaries samples were thermally etched. As it can be seen from SEM images, sample with lowest heating rate (50 °C/min) is more compact and dense. As presented in Figure 5.1 samples heated at the 150 °C/min and 200 °C/min are more porous compared to samples sintered using lower heating rates. (Red arrows).
At high heating rates the grains do not have enough time to grow and fill the gaps between them. However, at lower heating rates, grains have sufficient time to grow and create necking connections with each other. This leads to samples with higher density at lower heating rates and lower density at higher heating rates. Gaps between grains have been shown with red arrows and obviously, by lowering the heating rates vacancies can be reduced which can then result in density. Therefore, further studies were done based on the 50°C/min heating rate.

### 5.2.2 Density Measurements

Density of samples was measured using Archimedes method as explained in section 3.4.1.1. Results are presented in Figure 5.2. The highest densities were observed in samples sintered at 50 °C/min and 200 °C/min heating rates. The reported
theoretical density of pure barium titanate is 6.02 g/cm³ [83]. It can be seen that samples sintered with 50 °C/min at 1000°C for 3 min reached the 97.6% theoretical density.

![Figure 5.2](image)

**Figure 5.2.** Density of samples sintered with different heating rate at 1000 °C for 3 minutes.

The samples sintered at 100 °C/min reached 87.3% of BaTiO3 theoretical density. High heating rate which does not allow the grains to grow enough and fill the gaps between them. Samples sintered at heating rate of 150 °C/min and 200 °C/min reached relative density of 86.7% and 90.8% of BaTiO3 theoretical density, Based on these results heating rate of 50 °C/min was chosen as the optimal heating rate.

### 5.2.3 Grain size distribution

Grain size distribution graphs for all commercial samples are presented in Figure 5.3. Sample which was heated at 50 °C/min rate has more homogeneous distribution than samples at higher heating rates. In 50 °C/min samples, the grains are within size range of: 0.6 μm to 2.0 μm and frequency of distribution of grains with size 1 μm to 1.4 μm more or less are the same. Grain size distribution curve in sample sintered with heating
rate 100°C/min is broader than in sample heated to be ready for sintering with heating rate 50°C/min. Grains diameters in this sample are between 0.4 µm to 2.8 µm and grains with range size 0.8 to 1 micron occur with the highest frequency. In the sample sintered with heating rate 150°C/min grains size range is between 0.8 micron and 2.8 micron which similar to samples heated at 100°C/min rate. Samples heated at 200°C/min rate have the broadest range of grain sizes: from 0.6 micron to 3.2 micron. Samples sintered in SPS have smaller grains than industrial benchmark sample.

**Figure 5.3.** Grain size distribution of sintered samples with different heating rates
5.2.4 Chemistry and EDX analysis of Spark Plasma Sintered Samples

The EDX analysis was done on all as-sintered samples in order to check their elemental composition. It can be seen that the composition of sintered samples is matching EDX composition of sample D (compare section 4.4.1)

**Figure 5.4.** Concentration of elements Ca, Ti, Sr, Ba and Pb in samples sintered with different heating rates of 50, 100, 150 and 200 °C/min. HR- heating rate

Figure 5.5 shows the pie charts of elemental composition of sintered samples at different heating rates. In order to investigate concentration of various chemical elements (Ca, Ti, Sr, Ba and Pb) in the samples the EDX analysis was done at both high and low magnifications. As it is shown, the results of high and low magnification in all the samples are comparable. This shows that the elements are distributed homogeneously throughout the samples.
Figure 5.5. Chemical composition of the sintered samples with different heating rates (50, 100, 150 and 200 °C/min) at high and low magnification
5.2.5 Structure study by XRD pattern

The magnified images of doublet peaks at 2θ = 45° of samples with different heating rate, are illustrated in Figure 5.6.

![Figure 5.6](image)

**Figure 5.6.** The magnified image of doublet peaks at 2θ = 45° for (a) samples sintered at different heating rate before thermal etching, (b) samples sintered at different heating rates after thermal etching.

The area under the peaks is related to the quantity of the planes in the specific crystallographic direction. By comparing the area under the peaks in Figure 5.6 (a) it can be seen that the area under the peaks related to (200) plane, are decreased and the area under the (002) peaks are increased at higher heating rates. This is referred to the effect of high heating rate that does not give enough time the grains to grow. Also, it shows the preferential growth of the samples during SPS process in c-axis direction which is due to the uniaxial applied pressure during sintering process. The areas under the peaks and their ratios are shown in Table 5.3. The decrease in the ratios can be seen at higher heating rates before thermal etching.
Table 5.3. The area under the peaks of samples sintered at various heating rates.

<table>
<thead>
<tr>
<th>Heating rate</th>
<th>Before Thermal Etching</th>
<th>After Thermal Etching</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( A_{(200)} )</td>
<td>( A_{(002)} )</td>
</tr>
<tr>
<td>50 °C/min</td>
<td>85.21</td>
<td>54.17</td>
</tr>
<tr>
<td>100 °C/min</td>
<td>61.92</td>
<td>56.17</td>
</tr>
<tr>
<td>150 °C/min</td>
<td>60.31</td>
<td>101.84</td>
</tr>
<tr>
<td>200 °C/min</td>
<td>51.53</td>
<td>108.93</td>
</tr>
</tbody>
</table>

On the other hand, by thermal etching after sintering, a significant increase in the area under the (200) peaks is observed. This is happening because thermal etching is a process without applied pressure. This gives the grains the opportunity to grow in other crystallographic orientations. As a result the grains were able to grow in other crystal orientations. The \( A_{(200)}/A_{(002)} \) ratio after thermal etching shows the tendency of the grains for growing in directions other than c-axis during thermal etching. The growth in b-axis direction in samples sintered at higher heating rate were more than samples sintered at lower temperatures.

All of the X-ray diffraction patterns have characteristic peaks consistent with the International Centre for Diffraction Data (ICDD) files. As expected according to the dopants applied in powder processing, three compositions were matched with those spectra. First matched candidates for all four spectra related to different heating rates is \( \text{Ba}_{0.8}\text{O}_3\text{Pb}_{0.2}\text{Ti}_1 \) Barium Lead Titanium Oxide with ICSD file ref.no. 98-007-9217. Second matched candidate is \( \text{Ba}_{0.88}\text{Ca}_{0.12}\text{O}_3\text{Ti}_1 \) Barium Calcium Titanate with ICSD file ref.no. 98-002-9401 and the third candidate is \( \text{Ba}_{0.67}\text{O}_3\text{Sr}_{0.33}\text{Ti}_1 \) Barium Strontium Titanate with ICSD file ref.no. 98-002-4419. All the accepted candidates are crystallised in tetragonal crystal structure while \( \text{Ba}_{0.88}\text{Ca}_{0.12}\text{O}_3\text{Ti}_1 \) and \( \text{Ba}_{0.67}\text{O}_3\text{Sr}_{0.33}\text{Ti}_1 \) have P4mm symmetry and \( \text{Ba}_{0.8}\text{O}_3\text{Pb}_{0.2}\text{Ti}_1 \) have P4/mmm symmetry.
Figure 5.7. XRD pattern for doped Barium Titanate milled for 8 hours, calcined for 4 hours at 1100°C, milled for 8 hours, sintered at 1000°C for 3 minutes with different heating rates

5.2.6 Resistivity measurements

The resistivity of the sintered samples was measured using the setup described in section 3.4.1.2. The sample which showed the PTC was the one sintered at heating rate of 50 °C at 1000 °C for 3 minutes. Hence, this heating rate was selected as the optimal heating rate. In the next steps, series of experiments were done to investigate the effect of sintering temperature and holding time on the final properties of the samples.
5.3 Study the effect of different sintering temperatures

In this set of experiments, the impact of sintering temperature on microstructure was studied. Samples were sintered using following parameters: heating rate 50 °C/min, soaking time 3 minutes, pressure of 90 MPa at various heating temperatures: 800 °C, 850 °C, 900 °C, 950 °C and 1000 °C. The microstructural and phase analysis of the as sintered and thermally etched samples were done with SEM, EDX and XRD techniques.

In Table 5.4 images of sintered samples are shown. Samples sintered at lower temperatures are brighter than samples sintered at higher temperatures. On the other hand, all the samples got brighter after thermal etching at 1175 °C for 2 hours. This can be related to the redox environment in SPS furnace. As the samples is in a graphitic die which is placed in a vacuum chamber, the presence of oxygen is negligible.
However, after thermal etching the samples in a tube furnace with natural atmosphere, the samples were oxidised and the colour change can be attributed to this process.

Table 5.4. Pictures of as-sintered and thermally etched samples at different sintering temperature. Sintering parameters: Heating rate 50°C/min, soaking time: 3 minutes.

<table>
<thead>
<tr>
<th>Sintering temperature (°C)</th>
<th>Before Thermal Etching</th>
<th>After Thermal Etching</th>
</tr>
</thead>
<tbody>
<tr>
<td>800 °C</td>
<td><img src="image1.png" alt="Image" /></td>
<td><img src="image2.png" alt="Image" /></td>
</tr>
<tr>
<td>850 °C</td>
<td><img src="image3.png" alt="Image" /></td>
<td><img src="image4.png" alt="Image" /></td>
</tr>
<tr>
<td>900 °C</td>
<td><img src="image5.png" alt="Image" /></td>
<td><img src="image6.png" alt="Image" /></td>
</tr>
<tr>
<td>950 °C</td>
<td><img src="image7.png" alt="Image" /></td>
<td><img src="image8.png" alt="Image" /></td>
</tr>
</tbody>
</table>
5.3.1 Morphology and microstructure

Figure 5.9 shows the SEM images of the samples sintered at 800 °C, 850 °C, 900 °C, 950 °C and 1000 °C, respectively. To reveal grains and grain boundaries samples were thermally etched prior to SEM imageing (section 3.2.1.3).
Higher density of the samples was achieved in samples sintered at higher temperatures (see Figure 5.9). Figure 5.9(a) shows the samples sintered at 800 °C. It can be seen that grains are completely detached and no intergranular bonding has been formed. Comparing the shape of the grains with those at higher temperature, reveals that no grain growth was observed in samples sintered at 800 °C. In samples sintered at 850 °C, the intergranular bindings were partly developed. By increasing the sintering temperature up to 1000 °C the density of the samples were increased. This
was mostly because of the grain growth and the completely developed intergranular bindings. These observations were verified by density measurements mentioned in the next section.

5.3.2 Density measurements

Density samples sintered at different temperatures (800 °C, 850 °C, 900 °C, 950 °C and 1000 °C) were measured using Archimedes method as mentioned in section 3.4.1.1. Sample sintered at 1000 °C showed the highest density.

![Figure 5.10. Density of the sintered samples at various sintering temperatures (800 °C, 850 °C, 900 °C, 950 °C and 1000 °C)](image)

5.3.3 Grain size distribution

The grain size distribution graphs of samples sintered at different sintering temperatures are presented in Figure 5.11. The sample which was sintered at 800 °C has grain sizes in the range of 1.0-3.5 μm. A similar grain sizes and shape of distribution curve were observed in samples sintered at 850 °C. This shows that these two sintering temperatures were not high enough to overcome the diffusion barrier and let grain growth to happen. The grain size distribution in samples sintered at 900
°C and 950 °C was between 0.3-2.5 µm. Finally, for samples sintered at 1000 °C the grain sizes range was between 0.5-2.0 µm. The homogeneous grain size distribution of samples sintered at 1000 °C can be seen in Figure 5.9.

Figure 5.11. Grain size distribution of samples sintered at different sintering temperatures (800 °C, 850 °C, 900 °C, 950 °C and 1000 °C)
5.3.4 Chemistry and EDX analysis

The composition of the samples sintered at different temperatures (800 °C, 850 °C, 900 °C, 950 °C and 1000 °C) was studied using EDX analysis. (Figure 5.12) A significant drop in weight percentage of Pb can be seen in samples sintered at 900 °C. This can be related to the phase segregation happened at this sintering temperature which leads to transfer of Pb from the grains to the grain boundaries. In all other sintering temperatures the final chemistry matches that of the commercial benchmark.

![Figure 5.12](image.png)

**Figure 5.12.** Concentration of elements Ca, Ti, Sr, Ba and Pb in samples sintered with different sintering temperature of 800 °C, 850 °C, 900 °C, 950 °C and 1000 °C.

Figure 5.13 shows the comparison between high and low magnification EDX results of the samples sintered at various temperatures. The composition of the samples based high and low magnification EDX analysis were in excellent agreement with benchmark samples. However, this was not the case in samples sintered at 900 °C. As it can be seen, the weight percentage of Pb increased about 6.68 % at low magnifications compared to high magnifications. The most probable scenario is the phase segregation and migration of Pb to the grain boundaries.
Figure 5.13. High magnification and low magnification EDX analysis of the samples sintered at 800 °C, 850 °C, 900 °C, 950 °C and 1000 °C.
5.3.5 **Structure study by XRD pattern**

XRD pattern of the samples sintered at 800 °C, 850 °C, 900 °C, 950 °C and 1000 °C with heating rate of 50 °C/min and 3 minutes soaking time is illustrated in Figure 5.14. All the structures show the doublet peaks at 45° which are the characteristics of tetragonal structure at room temperature. The crystal structures were in agreement with that of the benchmark samples.

As expected according to the dopants applied in powder processing, three compositions were matched with those spectra. First matched candidates for all four spectra related to different heating rates is Ba$_{0.8}$O$_3$Pb$_{0.2}$Ti$_1$ Barium Lead Titanium Oxide with ICSD file ref.no. 98-007-9217. Second matched candidate is Ba$_{0.88}$Ca$_{0.12}$O$_3$Ti$_1$ Barium Calcium Titanate with ICSD file ref.no. 98-002-9401 and third candidate is Ba$_{0.67}$O$_3$Sr$_{0.33}$Ti$_1$ Barium Strontium Titanate with ICSD file ref.no. 98-002-4419. All the accepted candidates are crystallized in tetragonal crystal structure while Ba$_{0.88}$Ca$_{0.12}$O$_3$Ti$_1$ and Ba$_{0.67}$O$_3$Sr$_{0.33}$Ti$_1$ have P4mm symmetry and Ba$_{0.8}$O$_3$Pb$_{0.2}$Ti$_1$ have P4/mmm symmetry.
The XRD pattern of the samples after the thermal treatment was almost the same as the samples before thermal etching. The same phase composition was detected for the
samples after thermal etching. The only difference can be seen between the intensity and area under the peaks of the samples before and after thermal treatment. For this reason the magnified images of the doublet peaks at $2\theta = 45^\circ$ for the samples sintered at different sintering temperature is shown in Figure 5.16.

![Figure 5.16. The magnified image of doublet peaks at $2\theta = 45^\circ$ for (a) samples sintered at different sintering temperature before thermal etching, (b) samples sintered at different heating rates after thermal etching.](image)

The area under the peaks of these two planes are an indication for their growth direction under the pressure during SPS process and during thermal etching process can be seen in Table 5.5. It can be seen that by increasing the temperature from 800 °C to 1000 °C before thermal etching the proportion of the area under the peaks of $(A_{(002)}/A_{(200)})$ is decreased from 2.0 to 1.2. This shows the preferential grain growth in c-axis direction under pressure during SPS process. The proportion of the area under the peaks after thermal etching reveals that due to the lack of pressure during this process grains were able to grow freely in multiple directions. As a results the growth in a-axis direction was observed as the area under the peak of (200) plane is increased after thermal etching compared to as-sintered samples. Also, the shifting in the 2 theta
of the peaks at different sintering conditions can have several reasons. The most probable ones are mechanical strain and zero shifting of the non-calibrated instrument. In this case, the mechanical strain is most likely to happen because of the mechanical pressure applied during SPS process.

Table 5.5. The area under the peaks of samples sintered at different sintering temperatures.

<table>
<thead>
<tr>
<th>Samples with different sintering temperature</th>
<th>Before Thermal Etching</th>
<th>After Thermal Etching</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$A_{(200)}$</td>
<td>$A_{(002)}$</td>
</tr>
<tr>
<td>800 °C</td>
<td>111.25</td>
<td>57.19</td>
</tr>
<tr>
<td>850 °C</td>
<td>94.88</td>
<td>51.22</td>
</tr>
<tr>
<td>900 °C</td>
<td>67.57</td>
<td>37.92</td>
</tr>
<tr>
<td>950 °C</td>
<td>108.8</td>
<td>58.47</td>
</tr>
<tr>
<td>1000 °C</td>
<td>55.21</td>
<td>54.17</td>
</tr>
</tbody>
</table>

5.4 Study the effect of different soaking times

After optimising heating rate and sintering temperature in the next set of experiments the soaking time (dwell time) was studied. Following times were studied: 3, 5, 7 and 10 minutes. Sintering temperature and heating rate were fixed: 1000 °C, 50 °C/min. In the next section, the impact of various soaking times on microstructure of sintered samples.

In Table 5.6 pictures of the samples sintered at different soaking times before and after thermal etching are presented. All samples before thermal etching are darker than the samples after thermal etching. This is due to the oxidization that happens during the thermal etching process.
Table 5.6. General appearance of as-sintered and thermally etched samples at different sintering temperature.
Sintered 100°C, Heating rate 50 °C/min

<table>
<thead>
<tr>
<th>Soaking time (min)</th>
<th>Before Thermal Etching</th>
<th>After Thermal Etching</th>
</tr>
</thead>
<tbody>
<tr>
<td>3 minutes</td>
<td><img src="image1" alt="Image" /></td>
<td><img src="image2" alt="Image" /></td>
</tr>
<tr>
<td>5 minutes</td>
<td><img src="image3" alt="Image" /></td>
<td><img src="image4" alt="Image" /></td>
</tr>
<tr>
<td>7 minutes</td>
<td><img src="image5" alt="Image" /></td>
<td><img src="image6" alt="Image" /></td>
</tr>
<tr>
<td>10 minutes</td>
<td><img src="image7" alt="Image" /></td>
<td><img src="image8" alt="Image" /></td>
</tr>
</tbody>
</table>

5.4.1 Morphology and microstructure

Figure 5.17 illustrates changes of microstructure by increasing the soaking time from 3 minutes to 10 minutes. By increasing the soaking time, the intergranular diffusion is increasing and leading to more necking between the grains. Under such conditions,
due to the diffusion, larger grains grow bigger, while smaller grains get smaller and eventually disappeared. Highly packed sample was sintered at 3 minutes soaking time. Finally, at 10 minutes soaking time, regional melting of the grains and extensive grain growth happens.

Figure 5.17: SEM images of sintered at different soaking time (a) 3 minutes (b) 5 minutes (c) 7 minutes and (d) 10 minutes
5.4.2 Density measurements

Figure 5.18 illustrates the density of the samples sintered at 1000 °C with 50 °C/min heating rate for 3, 5, 7, and 10 minutes. Samples sintered for 3 minutes showed the highest density with 5.88 g/cm$^3$. Lower density was measured for samples with soaking times up to 7 minutes. This can be related to the growth of big grains while small one are disappearing. As a result, the packing of the system is decreased. By increasing the soaking time up to 10 minutes, local melting and exaggerated grain growth happens which increases the density of the samples.

Figure 5.18. Density of samples sintered at 1000 °C with 50 °C/min and different soaking times of 3, 5, 7 and 10 minutes.
5.4.3 Grain size distribution

Grain size distribution of the samples sintered at 1000 °C with heating rate of 50 °C/min and soaking time of 3, 5, 7, 10 minutes can be seen in Figure 5.19. Increase of the soaking time leads to the grain growth. For instance, grain sizes in the samples sintered at soaking time of 3 minutes is in the range of 0.6 µm to 1.8 µm. This range shifts to bigger grains: 0.5 µm to 2.5 µm for soaking time of 5 minutes. The same range was observed for 7 minute of soaking time while a significant shift to higher diameters of 1 µm to 5.5 µm.

Figure 5.19. Grain size distribution of samples sintered at 1000 °C, with 50 °C/min and different soaking times of 3, 5, 7 and 10 minutes.
5.4.4 Chemistry and EDX analysis

Figure 5.20 shows the chemical composition of the samples sintered at 1000 °C with 50 °C/min with different soaking times of 3, 5, 7 and 10 minutes. It can be seen that the chemical composition of the samples with soaking times of 3, 5 and 7 minutes are comparable with the benchmark composition. On the other hand, samples sintered for 10 minutes, had the lowest amount of Pb among all other samples.

This can be related to the phase segregation and migration of Pb to the grain boundaries. However, by comparing the results of high and low magnification EDX analyses, this theory seems unlikely to happen. As illustrated in Figure 5.21, the results of high and low magnification EDX are in good agreement for all samples. General elemental composition of all samples are almost the same. Also, the weight percentage
of the Pb in samples sintered for 10 minutes is around 1.2 - 3.18 for high and low magnifications. This verifies that no phase segregation has happened during sintering process as the elemental composition in both high and low magnification is in close agreement. In this case the most probable theory is the evaporation of Pb during the sintering process.
Figure 5.21. High magnification and low magnification EDX analysis of the samples sintered at 1000 °C with 50 °C/min at different soaking times of 3, 5, 7 and 10 minutes.
5.4.5 Structure study by XRD pattern

The XRD pattern of samples sintered at 1000 °C with 50 °C/min heating rate and 3, 5, 7 and 10 minutes soaking time before thermal etching can be seen in Figure 5.22. All samples were crystalized in tetragonal crystal structure. This is understood from the doublet peak at 45°. The XRD spectra of all samples are in agreement with industrial benchmark samples. Three phases of barium lead titanium oxide (Ba$_{0.8}$O$_3$Pb$_{0.2}$Ti$_1$), barium calcium titanate (Ba$_{0.8}$Ca$_{0.12}$O$_3$Ti$_1$) and barium strontium titanate (Ba$_{0.67}$O$_3$Sr$_{0.33}$Ti$_1$) were detected in as-sintered samples.

![XRD pattern of samples sintered at 1000 °C with 50 °C/min heating rate and 3, 5, 7 and 10 minutes soaking time before thermal etching.](image)

*Figure 5.22. XRD pattern of samples sintered at 1000 °C with 50 °C/min heating rate and 3, 5, 7 and 10 minutes soaking time before thermal etching.*
The XRD pattern of the samples after thermal etching process as mentioned previously is shown in Figure 5.23. The XRD pattern was observed to be exactly the same as that of the samples before thermal etching. However, the intensity and area under the peaks were changed which can be an indication of the grain growth direction before and after thermal etching.

![Figure 5.23. XRD pattern of samples sintered at 1000 °C with 50 °C/min heating rate and 3, 5, 7 and 10 minutes soaking time after thermal etching.](image)

Magnified images of the doublet peaks of samples sintered samples sintered at 1000 °C with heating rate of 50 °C for 3, 5, 7 and 10 minutes before and after thermal etching can be seen in Figure 5.24.
Comparing the area under the peaks of the samples sintered for different soaking times reveals the preferential growth of the grains in samples sintered for longer soaking times. It can be seen that at higher soaking times the ratio of \( A_{(200)}/A_{(002)} \) is decreased. This is regarded to the preferential growth of samples in \( c \)-axis direction which is mostly because of the uniaxial pressure during sintering process. This ratio has got bigger after thermal etching in air atmosphere. This is due to the free growth of grains in different direction during thermal etching process.

**Table 5.7.** The area under the peaks of samples sintered at 1000 °C with heating rate of 50 °C for 3, 5, 7 and 10 minutes before and after thermal etching.

<table>
<thead>
<tr>
<th>Samples with different soaking time</th>
<th>Before Thermal Etching</th>
<th>After Thermal Etching</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( A_{(200)} )</td>
<td>( A_{(002)} )</td>
</tr>
<tr>
<td>3 minutes</td>
<td>71.21</td>
<td>54.17</td>
</tr>
<tr>
<td>5 minutes</td>
<td>81.77</td>
<td>59.95</td>
</tr>
<tr>
<td>7 minutes</td>
<td>99.79</td>
<td>55.09</td>
</tr>
<tr>
<td>10 minutes</td>
<td>24.12</td>
<td>103.04</td>
</tr>
</tbody>
</table>
5.4.6 High Temperature XRD (Non-Ambient)

After studying the effect of different heating rates, sintering temperatures and soaking times, the sample with heating rate of 50 °C/min, soaking time of 3 minutes and sintering temperature of 1000 °C was selected for further microstructural studies. In this section, the tetragonal to cubic phase change (as mentioned in section 2.2.1.4.1) at Curie temperature in sintered samples was investigated by means of high temperature X-ray diffraction techniques.

Diffraction patterns were collected at room temperature at 25 °C, 100 °C, 200 °C and 300 °C, respectively. In order to check the reversibility of the phase transition, the last pattern was collected at room temperature (25 °C).

As it is depicted in Figure 5.25, the sample at 25 °C is crystalized in tetragonal crystal structure. The doublet characteristic peak of tetragonal phase at (002) and (200) at 45° was detected [80]. At 100 °C no significant change in the position and intensity of doublet peaks was observed. By increasing the temperature up to 200 °C the intensity of the peak related to (200) plane is decreased. At 300 °C the peak related to (200) plane is no longer present, but the (002) plane related to the cubic structure becomes dominant. For checking the reversibility of this phase transformation, the XRD pattern of samples after cooling to room temperature was also collected. The doublet peaks is clearly visible at room temperature verifying the presence of tetragonal structure.
Table 5.8. Area under the peaks of (200) and (002) planes of sample sintered at 1000 °C for 3 minutes with heating rate of 50 °C/min at various temperatures.

<table>
<thead>
<tr>
<th>Different temperatures for non-ambient XRD</th>
<th>( A_{(200)} )</th>
<th>( A_{(002)} )</th>
<th>( \frac{A_{(200)}}{A_{(002)}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>25 °C start</td>
<td>74.7</td>
<td>116.07</td>
<td>0.64</td>
</tr>
<tr>
<td>100 °C</td>
<td>179.77</td>
<td>119.78</td>
<td>1.5</td>
</tr>
<tr>
<td>200 °C</td>
<td>154.73</td>
<td>83.4</td>
<td>1.85</td>
</tr>
<tr>
<td>300 °C</td>
<td>253.43</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Table 5.8 shows the area under the XRD peaks of (200) and (002) planes of sample sintered at 1000 °C for 3 minutes with heating rate of 50 °C/min at four different temperatures. At elevated temperatures the \( \frac{A_{(200)}}{A_{(002)}} \) ratio is increased. Which shows the higher population of (200) planes compared to (002) planes. This is due to the phase transition from the tetragonal at temperatures below 200 °C to cubic above 200 °C temperature.
For the purpose of comparison the phase transition in industrial benchmark sample was also investigated. It was observed that the phase transition from tetragonal to cubic starts at around 200 °C. The phase transition is completed at 300 °C. The reversibility of the phase transition was also checked by collecting XRD spectrum of the same samples at room temperature (25 °C). It can be seen that the doublet characteristic peak of tetragonal phase is present. This pattern was also observed in all samples sintered at 1000 °C for 3 minutes with 50 °C/min heating rate (Figure 5.26).
Chapter 6: Conclusions

In current research, intensive microstructural and structural analyses was used to study some industrial barium titanate PTC samples. Then, based on the obtained results, barium titanate doped powder was synthesized via solid state synthesis route. This method effectively produced a doped barium titanate powder which was then consolidated into dense, highly crystalline ceramic samples. For this purpose, spark plasma sintering (SPS) method was used. In order to investigate the effect of sintering parameter, various samples were sintered with different parameters such as heating rate, sintering temperature and soaking time. The effect of these parameters on the final microstructural and structural properties of the samples was analysed. As a result, the optimal sintering conditions were established for doped barium titanate.

XRD Analyses of the industrial samples revealed their highly crystalline and homogeneous crystal structure. All the samples showed tetragonal crystal structure at room temperature. Three different phases of $\text{Ba}_{0.8}\text{O}_3\text{Pb}_{0.2}\text{Ti}_1$ Barium Lead Titanium Oxide, $\text{Ba}_{0.88}\text{Ca}_{0.12}\text{O}_3\text{Ti}_1$ Barium Calcium Titanate and $\text{Ba}_{0.67}\text{O}_3\text{Sr}_{0.33}\text{Ti}_1$ Barium Strontium Titanate were detected. The grain size distribution of the samples showed a wide range between 2-8 µm. EBSD technique verified that there was no preferential orientation in industrial samples, but some local orientation was observed. This is because no external electrical field was applied to tested samples and they were weakly polarized. SEM and EDX analyses approved the difference in thickness of conductive layers and elemental composition of the conductive layer and the bulk substrate of the industrial samples. The electrical resistivity variations versus temperature of all industrial samples were measured and the lowest discrepancy among the resistivity measurements was observed in sample D specimens. According to these results,
sample D was selected as benchmark. Barium titanate doped powder were prepared based on the chemical composition of the sample D. The effect of various parameters of SPS was studied.

The XRD study showed the tetragonal crystal structure for all samples at room temperature. Also, presence of three different phase compositions of $\text{Ba}_{0.8}\text{Pb}_{0.2}\text{Ti}_1$ Barium Lead Titanium Oxide, $\text{Ba}_{0.88}\text{Ca}_{0.12}\text{Ti}_1$ Barium Calcium Titanate and $\text{Ba}_{0.67}\text{Sr}_{0.33}\text{Ti}_1$ Barium Strontium Titanate in all SPS sintered samples were detected. XRD analysis revealed the preferential grain growth in samples after spark plasma sintering which was related to the high applied pressure during the sintering process. However this preferential grain growth seemed to be disappeared gradually after the thermal etching process. Analyses of the synthetic doped barium titanate samples produced by spark plasma sintering revealed the synthesis of highly crystalline and homogeneous ceramic samples. It was revealed that the lowest heating rate of 50 °C/min results in the samples with highest density and the most homogeneous grain size distribution. Also, the sintering temperature of 1000 °C were chosen to be the optimal sintering temperature based on the SEM, grain size distribution analysis and density measurements. Furthermore, studying the soaking time showed that the samples sintered with soaking time of 3 minutes have the optimal density and grain size distribution. The resistivity of all the sintered samples was measured while the only sample that showed the PTC effect was the sample sintered at 1000 °C, for 3 minutes with heating rate of 50 °C/min. This was in complete agreement with the expected results based on the microstructural characteristics of these samples. The non-ambient temperature XRD showed the phase transition from tetragonal crystal structure at room temperature to cubic crystal structure at the temperature higher than 200 °C for the sample sintered at 1000 °C, for 3 minutes with the heating rate of 50 °C.
/min. This was in good agreement with the non-ambient temperature XRD results of the industrial sample D as a benchmark.
References


Appendices

Appendix A: Chapter 4

EDX Results

EDX images and pie charts for sample B to H (in conductive layer and bulk of original samples)

Sample B:

**High mag EDX for conductive layer sample B**

<table>
<thead>
<tr>
<th>Element</th>
<th>Percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>0.09%</td>
</tr>
<tr>
<td>Ca</td>
<td>1.52%</td>
</tr>
<tr>
<td>Ti</td>
<td>3.24%</td>
</tr>
<tr>
<td>Sr</td>
<td>0.48%</td>
</tr>
<tr>
<td>Ba</td>
<td>26.1%</td>
</tr>
<tr>
<td>Pb</td>
<td>53.97%</td>
</tr>
</tbody>
</table>

**High mag EDX for bulk sample B**

<table>
<thead>
<tr>
<th>Element</th>
<th>Percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>0.48%</td>
</tr>
<tr>
<td>Ca</td>
<td>2.26%</td>
</tr>
<tr>
<td>Ti</td>
<td>15.62%</td>
</tr>
<tr>
<td>Sr</td>
<td>1.56%</td>
</tr>
<tr>
<td>Ba</td>
<td>53.97%</td>
</tr>
<tr>
<td>Pb</td>
<td>15.62%</td>
</tr>
</tbody>
</table>
Sample C:

Conductive layer

Bulk

High mag EDX for conductive layer sample C

High mag EDX for bulk sample C

<table>
<thead>
<tr>
<th>Element</th>
<th>Conductive Layer</th>
<th>Bulk</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>28.59</td>
<td>13.25</td>
</tr>
<tr>
<td>Ca</td>
<td>4.29</td>
<td>13.25</td>
</tr>
<tr>
<td>Ti</td>
<td>2.34</td>
<td>25.36</td>
</tr>
<tr>
<td>Sr</td>
<td>1.92</td>
<td>0.98</td>
</tr>
<tr>
<td>Ba</td>
<td>1.68</td>
<td>56.13</td>
</tr>
<tr>
<td>Pb</td>
<td>65.44</td>
<td></td>
</tr>
</tbody>
</table>
Sample D:

High mag EDX for conductive layer sample D

- Al: 0.56
- Ca: 0.33
- Ti: 0.23
- Sr: 14.85
- Ba: 84.03

High mag EDX for bulk sample D

- Al: 3.8
- Ca: 1.11
- Ti: 26.74
- Sr: 7.8
- Ba: 58.8
- Pb: 1.74
Sample E:

**Conductive layer**

**Bulk**

High mag EDX for conductive layer sample E

- Al: 87.94%
- Ca: 10.82%
- Ti: 0.9%
- Sr: 0.19%
- Ba: 0.16%
- Pb: 0.69%

High mag EDX for bulk sample E

- Al: 59.31%
- Ca: 11.91%
- Ti: 26.33%
- Sr: 0.3%
- Ba: 0.69%
- Pb: 1.46%
Sample F:

High mag EDX for conductive layer sample F

High mag EDX for bulk sample F
Sample G:

Conductive layer

Bulk

High mag EDX for conductive layer sample G

High mag EDX for bulk sample G
Sample H:

Conductive layer

Bulk

High mag EDX for conductive layer sample H

High mag EDX for bulk sample H

Electron Image 1
EBSD Results

Sample B:
Sample C:
Sample D:
Sample E:
Sample F:
Sample G:
Sample H: