PTCR Effect in La_2O_3 doped $BaTiO_3$ Ceramic Sensors

By

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Abstract

The positive temperature coefficient of resistivity (PTCR) sensors is resistor materials that undergo a sharp change in resistivity at a designed Curie temperature due to its unique structure and chemical composition. This effect serves important control functions in a wide variety of electronic circuitry and similar applications. Conventional calcining of mixed oxides method (CMO) is used for fabricating lanthanum doped barium titanate ($BaTiO_3$) for PTCR behaviour through solid-state-sintering route, at 1100°C, 1350°C. Two batches of samples were fabricated at low and high sintering temperatures of 1100°C, 1350°C respectively. The effect of different concentrations of donor dopant on $BaTiO_3$ on the electrical properties of $Ba_{(1-x)}La_xTiO_3$ with x= 0.0005, 0.001, 0.002, 0.0025, 0.003 mol%, is investigated at low sintering temperature. The influence of lantanum doping with $Al2O_3$+SiO_2+TiO_2 (AST) as sintering aids on the electrical properties of $Ba_{(1-x)}La_xTiO_3$ with x= 0.0005, 0.001, 0.003 mol%, is also investigated. The results of the electrical characterization for the first batch of samples showed an increase in room temperature resistance with increaisng donor concentration. Also the results of the electrical characterization for the second batch of samples also showed the same increase in room temperature resistance with increasing donor concentration. For first batch of sensors the high room temperature resistance keeps the jump small and these materials showed V-shaped NTCR-PTCR multifunctional cryogenic sensor behavior with a strong negative coefficient of resistance effect at room temperature.

Where as the second batch of sensors showed few orders of magnitude rise in resistivity values. The La-doped $BaTiO_3$ ceramics co-doped with Mn gives an enhanced PTCR effect which can be exploited for various sensor applications.

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Chapter 1

Introduction

1.1 Background

The present research focuses on developing a smart ferroelectric, semiconducting sensor materials which has positive temperature coefficient of resistivity (PTCR) characteristics. Smart PTCR thermistor materials are thermally sensitive resistors, and can be manufactured from an insulating barium titanate ($BaTiO_3$) by adding small amounts of dopants. Because of its technical importance and difficulty in explaining the behavior thoroughly, the study of electrical properties of $BaTiO_3$ is still a very important research topic in the research community. The electrical resistance and ferroelectric transition temperature can be controlled effectively by doping in either the barium or titanium site with proper donor impurity ions. Ceramic materials are preferred over polymeric materials due to their wide range of switching temperatures, longer working life, better thermal stability, high reliability and low room temperature resistivity values. However it is difficult to use in low voltage applications. The area of PTCR research is very wide and it has been the center of attention of research in science and engineering during last 50 years. Various researches have tackled these materials from different perspectives. These can be categorized under specific topics such as:

- Ferroelectric Ceramics
- Spontaneous polarization
- Positive Temperature Coefficient of Resistance ceramics
- Defect chemistry

- Grain and Grain boundary segregation effect etc.

Semi conducting $BaTiO_3$ ceramic materials with low room temperature resistivity and high PTCR performance is one the most attractive material for industrial applications especially in electronic devices. The following are some of the industrial applications of PTCR ceramics:

- PTCR Thermistors for over current protection – Ceramic PTCR thermistors are used instead of conventional fuses to protect loads such as motors, transformers, etc. or electronic circuits against overcurrent. As opposed to PTC thermistors made of plastic materials, ceramic PTC thermistors always return to their initial resistance value, even after frequent heating/cooling cycles. It is also used in telecommunication applications, where over voltage and over current can result from surges due to direct light striking, induction between power lines and phone lines where the PTCR elements can moderate the disturbance by using a re-settable device such as PTC thermistor.
- PTCR thermistors for Television degaussers (Transient Current Generators)- PTCR themistors can be used for picture tube degaussing, where the PTC thermistors degauss the shadow mask of the color pictures tubes by reducing the alternating current flowing through the degaussing coil within short period of time and where a large inrush current and residual current is crucial for good degaussing.
- Temperature controlled Heaters - PTCR ceramic materials when operated in the region of the Curie temperature, they will maintain an almost static temperature with large variations in ambient temperature and voltage. They are used as self thermostatting controls, *e.g.*, heating elements for hair dryers and domestic heaters.

- PTCR thermistors for motor starting- Single-phase induction motors (*e.g.* in compressors for refrigerators and air conditioners) can effectively be started when an auxiliary coil is used in the starting phase.
- PTCR thermistor sensors (*e.g.* Level sensors) - A PTC thermistor is used as a sensor when the influence of environmental conditions (*e.g.* temperature) on the electrical characteristics. Thermistors when heated with low voltage (~12 V) respond to a change in external cooling conditions by changing its power consumption. At a constant voltage the power consumption is a measure of dissipation condition, where with increasing dissipation the thermistor cools down and the current rises due to the PTCR element. Increase in current occurs when a PTCR thermistor is heated in air and is immersed into a liquid, where a large amount of heat dissipation occurs in liquid than in air. This will make the PTCR sensor an ideal candidate for over flow control liquid level sensors.
- PTCR sensors for motor and machine protection- PTCR thermistors are widely employed as temperature sensors in electrical machines to monitor the winding temperature.

1.2 Objectives

At the start of this research it was felt a comprehensive and thorough literature survey will support our research and identify further area which needs to be identified. Even though research on this topic is not new in ceramic sensor manufacturing technology, there are still so many aspects of PTCR effect that requires further clarification and understanding.

(1) Since this is a new area of research within our research group, the first objective is to conduct a comprehensive and thorough survey of literature is done on the topic of this research. This will include ferroelectric ceramics, peroviskite structure, PTCR

ceramics, defect chemistry, effect of donor, acceptor additives on electrical properties, effect of sintering aids and processing characteristics.

(2) Prepare a ceramic sensor with low sintering temperature.

(3) Prepare a ceramic sensor with low room temperature resistivity with semi conducting behavior.

(4) Improving the PTCR effect with additive free sensor materials with good reproducible PTCR properties.

(5) Use various characterization techniques to identify the specific characteristic of the sensors.

In chapter 2, a literature review on ceramic semi-conducting materials was undertaken for a comprehensive and thorough understanding of PTCR behavior of ceramics. In chapter 3, the experimental methodology for the preparation of PTCR $BaTiO_3$ materials are presented. The material fabrication techniques and the measurement techniques such as XRD for crystallographic analysis and phase formation, resistivity measurements, scanning electron microscopy (SEM), Energy dispersive spectroscopy (EDS) analysis, and Impedance spectroscopy measurements were discussed. In this study two batches of the samples were examined for PTCR behavior. First batch of samples prepared with La_2O_3 doped $BaTiO_3$ with out any sintering aids and PTCR enhancers. Second batch of samples were prepared with La_2O_3 doped $BaTiO_3$, co-doped with acceptor MnO_2 along with liquid phase sintering aids (AST) were determined PTCR behavior. To reduce the room temperature resistivity and to stabilize the electrical properties, a novel secondary thermal treatment method was also used for samples. In chapter 4, the results are presented and are discussed in relation to the application of these materials as PTCR sensors. Chapter 5 discusses the conclusion and recommendations for further work needed for develop a semi conducting $BaTiO_3$ ceramic with PTCR behavior.

Chapter 2

PTCR Effect and Literature Review

2.1 Ferroelectric Ceramics

Comprehensive and thorough literature review on PTCR ceramic Semiconducting materials is conducted in this chapter. The permanent electric dipole moment of some materials, in certain cases can be reoriented by the application of electric field. Such materials are called ferroelectric materials and this spontaneous polarization disappears at certain temperature or Curie temperature.

Ferroelectricity was discovered in the early 1920's and the early ferroelectric ceramics were made from $BaTiO_3$ used to develop capacitors with high dielectric constant [1]. Ferroelectric ceramics are compounds of metallic and nonmetallic oxides. Ferroelectric crystals are a section of large class of materials called pyroelectrics. A pyroelectric material has property that the single crystal with no surface charges is polar. Ferroelectric crystals are those crystals which exhibit spontaneous polarization that is electric polarization without any external electric field. When an electric field is applied to ferroelectric materials they deform, polarize and when mechanically stressed they form a special class of materials.

They also develop the piezoelectric responses such as strain, electric displacement when they are subjected to electric field, mechanical stresses and become nonlinear with significant hysteresis behavior under cyclic electric loading. This nonlinear behavior can be attributed to domain switching mechanism. This special class of materials is called piezoelectric material. They are widely used as transducing materials in sensing and actuating devices in smart systems.

Polycrystalline ferroelectric materials are composed of large number of randomly oriented grains, and each grain is made up of various numbers of domains, which in turn composed of a number of unit cells. At higher temperatures these materials become non-polar, where the cells of cubic symmetry in which the centers of positive charge and negative ionic charges coincide. However, at temperature lower than Curie temperature, their centers of positive and negative charges coincide and make a separation between the charges and form a dipole moment. Ferroelectricity arises from those materials which contain electric dipoles, where an increased polarization results in increase in local field, also known as the Mosotti field [2]. This spontaneous polarization is found only in relatively small group of materials whose crystalline structure is characterized by the absence of centre of symmetry and by the presence of one or more polar axis [3]. Due to lack of centre of symmetry in ferroelectric materials the center of positive charge does not coincide with the center of negative charge [4]. Ferroelectric crystals possess high dielectric constant values, they also show dielectric anomalies i.e., the dielectric constant reaches a maximum value at the transition temperature called the Curie point.

The crystal is ferroelectric below the Curie point and above the transition temperature the crystal becomes paraelectric in nature Ferroelectric materials exhibit more than one phase transition temperature and were evident by anomalies in thermodynamic properties such as specific heat, elastic modulus, expansion coefficient, and structural changes [5].

The transition from the paraelectric to the ferroelectric phase is accompanied by a structural and therefore a dimensional change, where the materials will experience strains. These changes are accompanied by stresses, in the multi domain structures within the crystals or grains. Ferroelectric crystals are classified into, order-disorder type and displacive type. Order-disorder ferroelectrics have permanent dipoles randomly oriented above the transition temperature and become ordered below T_c. In displacive ferroelectrics, the spontaneous polarization occurs due to a displacement of certain ion in the ferroelectric transition temperature. The displacive type such as many perovskite is the most important class of ferroelectrics [6]. There are number of perovskite structured ferroelectrics like calcium titanate ($CaTiO_3$), barium titanate ($BaTiO_3$), lead titanate ($PbTiO_3$), lithium niobate ($LiNbTiO_3$) etc., used in various number of electrocearmic applications.

2.2 Perovskite Structure

A perovskite structure consists of 12-coordinated A^{+2} atoms on the corner, octahedral oxygen (O^{--}) ions on the faces and the tetrahedral B^{+4} in the center. The name comes from the mineral $CaTiO_3$, an ABO_3 type mixed oxide which exhibit this structure. The simple cubic perovskite structure, which is the high temperature form for many mixed oxides of the ABO_3 type, is shown in the figure 2.1.

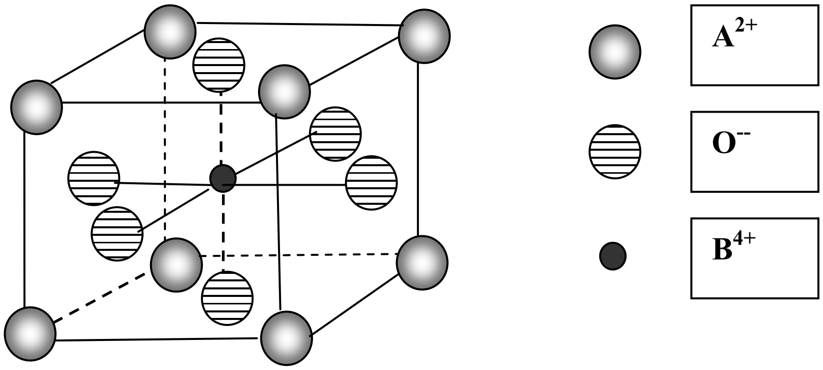


Figure 2.1. Perovskite Structure-type ABO_3.

This is one of the first simple structures to exhibit compounds with ferroelectric properties and is still probably the most important ferroelectric prototype [7]. Perovskite structures have the curious property that the central tetrahedral B^{+4} atoms does not touch it coordination neighbors in violation of Pauling's rule. This allows small displacement of the atoms that lead to the distortion of the structure and the reduction of symmetry giving it the property of ferroelectricity and will have profound effects on physical properties; perovskite structure materials play an important role in dielectric ceramics [8].

The ferroelectric tetragonal and perovskite cubic structures of barium titanate are shown in the Figure.2.2, Figure.2.3 respectively. In perovskite structured $BaTiO_3$, barium ions are located at the corners, the titanium ion is located at the center and the oxygen ions are located at the face center of the cubic lattice cell. Each barium ion is surrounded by 12 oxygen ions and each titanium ion is surrounded by 6 oxygen ions and each oxygen is surrounded by 4 barium and 2 titanium ions.

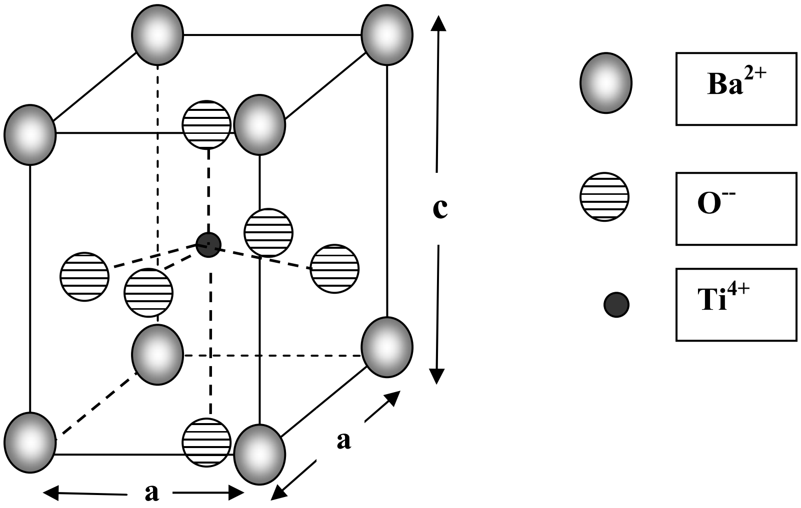


Figure 2.2. Tetragonal crystal structure of $BaTiO_3$ at room temperature [12].

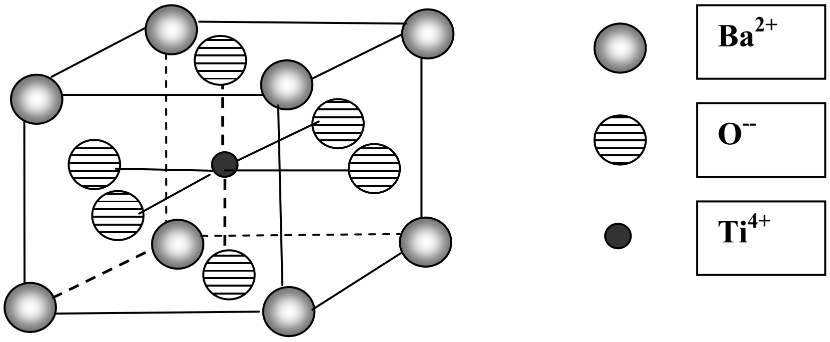


Figure 2.3. Cubic (m3m) crystal structure of $BaTiO_3$ above T_c [2].

Barium titanate is in its tetragonal (ferroelectric) phase at room temperature and will transform into cubic (paraelectric) phase above its Curie temperature (Tc~120^{0}C). In tetragonal ferroelectrics two types of domain boundaries exists, 90° and 180°. In some ferroelectric materials a sharp transition between the ferroelectric and paraelectric phases is not observed. Such materials are said to have diffuse phase transition (DPT) [9]. Ferroelectric materials which exhibit DPT are termed ferroelectric relaxors and are frequency dependent.

According to Mertz [10,11], the dielectric values for single domain $BaTiO_3$ crystals measured perpendicular (ϵ_a) to the polar axis are greater than that of the measured parallel (ϵ_c) to the polar axis at room temperature and above the Curie point the crystal is cubic ($\epsilon_a = \epsilon_c$). This discrepancy is explained by the optical observations that are the Ti ions in the oxygen octahedral have an increasing tendency to displace itself from the eccentric position (001) towards (011).

An analogous dielectric behaviour is observed in the temperature range of 0°C to -85°C and here the stable position of Ti ions in the oxygen octahedral seems to become the direction of body diagonal (111). The dielectric constant values of the single domain $BaTiO_3$ crystal is shown in the figure 2.4.

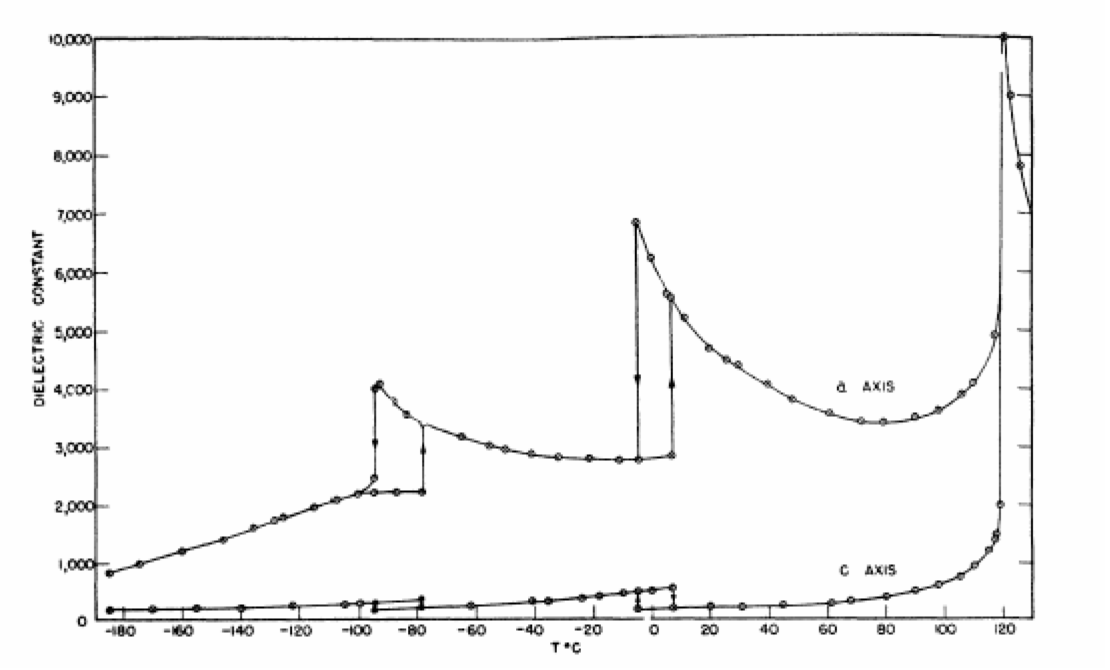


Figure 2.4. Dielectric Constant as a function of temperature [10].

As the crystal transition occurs from cubic to tetragonal phase each unit cell in the crystal becomes polar with 1% approximate lattice constant shift. This change in the lattice structure will bring spontaneous polarization with an abrupt increase in the dielectric constant values [4].

Above the Curie temperature this dielectric constant (Єr) decreases with an increase in temperature described in terms of Curie-Weisis law.

$$\epsilon r = C/ (T-\theta) \qquad (2.1)$$

Where, C is the Curie constant = 1.5 X10^5 for $BaTiO_3$

T is the absolute temperature

Θ is the Curie-Weiss temperature = 383K

Barium titanate is an insulator that can be made into an n-type semiconducting either at reducing atmosphere – oxygen vacancies or at donor doping. N-type conductivity in $BaTiO_3$ can be achieved by partially reducing Ti^{+4}, and where delocalization of electrons at room temperature takes place [4]. Ti^{+4} can be reduced according to the following formula.

$$\mathbf{Ti^{+4} + e^{-} \longrightarrow Ti^{+3}} \qquad \mathbf{(2.2)}$$

Saburi [14] proposed an electron hoping conduction model for reduced $BaTiO_3(1-x)$ to explain conductivity mechanism in semiconducting barium titanate, where the hoping of electrons from one titanium ion to another, i.e. from Ti^{+3} and Ti^{+4} takes place. Conductivity mechanism is also explained in titanium reducing process and the polaron theory proposed by Gerthsen *et al.'s* [15].

2.3 Positive Temperature Coefficient of Resistance (PTCR) ceramics

The behavior change in the electrical resistivity of a doped polycrystalline $BaTiO_3$ at ferroelectric transition temperature (Tc) is commonly denoted positive coefficient of resistance effect (PTCR) [16] and was first reported by Haanyman *et al.* [16], in their German patent in the early year of 1955.

Different theories have been proposed to explain PTCR effect at its Curie temperature (Tc). Most of the models are based on an assumption that the grain boundaries exhibit special properties and that they differ from those of their bulk properties. Sauer *et al*. [17], was the first reported model on PTCR and was then explained by Heywang [4, 27] in terms of potential barriers. Since then various studies on barium titanate was made to fully understand the mechanism of the PTCR effect.

In general the difference between an ordinary and a "smart" material can be demonstrated through PTCR effect. PTCR ceramics can be regarded as typical smart materials which sense temperature and send electrical signal as feed back [18]. PTCR behavior in polycrystalline barium titanate is shown in figure 2.5. $BaTiO_3$ is an insulator in its pure form with a narrow band gap energy (~3.1 eV) and a room temperature resistivity of more than 10^{10} Ω cm [4].

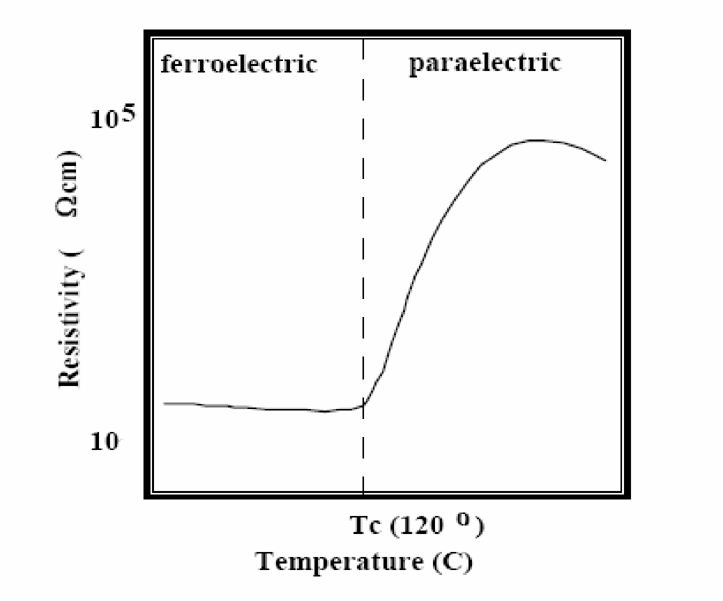


Figure 2.5. Schematic diagram for a typical resistivity vs. temperature curve for semi conducting polycrystalline $BaTiO_3$ with PTCR behavior [19].

The significant nonlinear change in electrical resistance in donor doped $BaTiO_3$ has been modeled as a combination of ferroelectricity, semiconductivity and grain boundary resistive effects [20]. It is well known that semiconducting polycrystalline $BaTiO_3$ can only produce PTCR with non-linear anomalous increase in resistivity above Curie temperature.

The ferroelectric properties of $BaTiO_3$ require that the orientation of the polar axis depends upon applied electric field strength which results in marked changes in the intensity of the X-ray scattering of some crystallographic planes. Such orientations are directly observed in single crystals, [21].

In the early years of PTCR studies, the voltage dependence characteristics for some valence controlled barium titanate were explained by Sauer *et al.* [17]. Similar studies were made by Harman [22] when unusual electrical properties in samarium doped $BaTiO_3$ were observed in crystallographic transitions. Also, electrical resistivity almost independent of temperature behaviour is witnessed in the tetragonal region. The effect of resistivity on different additives was studied by Saburi [14], and was used to explain the valence controlled mechanism for the PTCR effect in barium titanate. Resistivity of insulating barium titanate in higher orders of magnitude is drastically controlled by suitable valence replacement. According to Saburi, the valence controlled mechanism of barium titanate is that whose room temperature resistivity is of the order of $10\text{-}10^4$ ohm-cm shows anomalous positive character of temperature dependent resistivity.

Känzig [23], have suggested that the PTCR effect is due to the surface charge layers formed at grain boundaries of ferroelectric materials. In case of a semiconductor, these space charged layers formed at the surface of the ferroelectrics arises from the trapping of electrons [24]. Using Heywang's [4, 27] space charge barrier layer model, the work function, with respect to temperature measurements were made by J.Holt [25]. However above transition temperature their behavior becomes complicated due to desorption of gas from the surface.

Grain boundary resistance is a well known effect in polycrystalline oxide semiconductors [26], especially in n-type semiconducting materials where trapping of electrons takes place by adsorbing oxygen atoms either physically or chemically. The PTCR behavior in semiconducting $BaTiO_3$ was explained by the conduction model of Heywang and Jonker [27, 28] and originates from the temperature dependent potential barriers arising at the grain boundaries [29]. The high resistance of semiconducting $BaTiO_3$ at elevated temperature with increasing field strength is due to grain boundary resistance. This high resistance is totally concentrated at the blocking layer due to surface effects in the ceramics [28]. The same type of effect was observed in Saburi's [13, 14] investigations.

From experimental studies done by Jonker [28, 114,141,152], it is believed that grain boundary resistance is the result of non-equilibrium oxidation and is much stronger in $BaTiO_3$ than the other oxides. Research by MacChesney *et al.* [30] showed valence controlled mechanism failed to explain the sudden rise in resistivity at Curie temperature and it continued in the temperature range ~ 90°C to 175°C.

Hall measurements for semiconducting materials using an ac sample current method were not successful in Saburi's experiment [14], due to strong noise effects with very small e.m.f values. Also inaccurate Hall constant values are obtained and the temperature measurement could not extend beyond 70°C. A successful Hall measurement for PTCR effect were obtained for semiconducting barium titanate ceramics near the ferroelectric Curie temperature by Ryan and Subbarao [31], and found that the PTCR effect is due to a loss in the number of carriers in the intergranular region near transition temperature.

In general, the PTCR effect is observed only in polycrystalline ceramics, and is not observed in single crystals or p-type semiconducting materials. Experimental investigations by Saburi and Wakino [13] on butterfly type single crystals grown under valence controlled mechanism don't bring a resistivity anomaly. Measurements using 2 probe and 4 probe method were under taken by Udea and Ikegami [32] on the same single crystal. PTCR effect was shown in the former case but not in the latter case.

To further understand the PTCR mechanism in single-grain $BaTiO_3$ crystals several researchers [33-34], have used different experimental techniques to measure PTCR characteristics. Their researches have shown that there exists a grain boundary without anomalous resistivity and PTCR behaviour with I-V characteristics. Although different techniques were used, they obtained almost similar results.

Three different types of resistance-temperature characteristics in single grain crystals with PTCR anomalies were identified by Kuwabara *et al.* [35, 36]. Below the Curie temperature (T_c) donor doped $BaTiO_3$ materials will have low electrical resistance values due to semiconducting n-type polaron conduction behaviour. A relatively low room temperature resistance with large change in higher orders of resistance in order to optimize the electrical properties of the materials is recognized in PTCR materials technology.

2.4 Defect chemistry

In this section the defect chemistry of stoichiometry and non-stoichiometry of undoped and donor doped $BaTiO_3$ with charge compensation mechanism and effect of oxygen partial pressure on bulk sample will be discussed. According to Verwey's controlled valence method [16], ferroelectric compound $BaTiO_3$ can be transformed into a semiconductor by partly replacing Ba^{2+} by large trivalent ions or partly replacing Ti^{4+} ions by large pentavalent ions. The doping elements are chosen from those elements which have ionic radii similar to that of either Ba^{2+} or Ti^{4+}. Sauer and Flaschen [17] reported that higher valent cation is the only effective replacement for host ions to produce semiconducting materials.

In all cases the extra positive charges in the foreign ions are compensated by electrons which are assumed to be present in the Ti-3d conduction band [37]. Stoichiometric barium titanate with wide energy band gap is considered to be an insulator with a room temperature resistivity of the order of more than 10^{10} Ω cm. Variations in the energy band gaps are observed with the measurements of electrical conductivity [38], and optical absorption band edge observations [39].

The defect chemistry in crystalline undoped and doped $BaTiO_3$ have been studied with many differences in experimental and theoretical observations for La doped $BaTiO_3$ have been studied by many researchers [40-45].

Studies on doped $BaTiO_3$ by Jonker [28] showed that, the compensation of the foreign ions by electrons is only present at lower concentrations and at higher concentrations a gradual transition to vacancy compensation occurs. Nature of charge carriers in $BaTiO_3$ were determined by the Hall effect and Seebeck coefficient measurements [44]. Lewis and Catlow have used [45], computer simulation technique, to study the defect chemistry in doped and undoped $BaTiO_3$. Consistent electrical conductivity measurement is observed in the temperature range of 25°C-1300°C and oxygen partial pressure (P_{O2}) of 10^{-20} to 1 atmosphere. Daniels and Härdtl [40], found that an excess of cation vacancies near the grain boundaries act as an acceptor and form a depletion layer.

Physical properties of the crystalline solids depend on the presence of native or foreign point defects. For pure compound crystals the native defects are: a) Atoms missing from the lattice sites and are known vacancies, b) Atoms present at sites where atoms should not be in general called interstitials and c) Atoms occupying sites normally occupied by other atoms or misplace atoms [46]. In addition there may be defects in the electronic structure such as quasi-free electrons in the conduction band or electrons missing from the valence band called holes. Solid solutions of aliovalent impurities and deviations from stoichiometry lead to the presence of point defects in crystalline organic compounds and the defects can be either ionic or electronic in nature [47].

From the investigations of Daniels and Härdtl [40], it was observed that, the electron concentration is equal to that of the donor dopant concentration only at a limited range of oxygen partial pressures, as shown in the figure.2.6. At low oxygen partial pressure, lanthanum is electronically compensated and at higher oxygen partial pressure lanthanum is ionically compensated.

Barium vacancies are favorable and also responsible for ionic compensation mechanism, while titanium vacancies are energetically unfavorable for ionic compensation [48, 49]. At higher oxygen partial pressures the undoped materials exhibit p-type conductivity, and will ignore the presence of interstitial defects, defect clusters, which gradually changes into n-type conductivity at low oxygen partial pressures [50]. The conductivity of the n-type material is determined mainly by oxygen vacancies. This barium vacancy concept [40] has been disputed in some regards, since it could not explain the Hall Effect measurements, I-V characteristics of single grain boundaries.

Even at excess titanium composition, excess barium layers were observed at grain boundaries compositions using combination of Scanning Auger Electron Spectroscopy and Argon ion sputtering on fractured samples under vacuum [51]. Large PTCR effect is observed for porous $BaTiO_3$ with Ba- rich compositions [52]. Jonker proposes [28, 114, 141,152] that acceptor states at the grain boundaries are due to chemisorbed oxygen species, rather than cation vacancies.

Earlier research on thermodynamic investigations [50], have shown, that there exists no defects other than only neutral and single or double ionized (positively charged) oxygen vacancies (V_O, $V_O^{\bullet}$,$V_O^{\bullet\bullet}$). Neutral and single or double ionized (negative charge) barium vacancies (V_{Ba}, V_{Ba}',V_{Ba}'') are shown in figure 2.6.

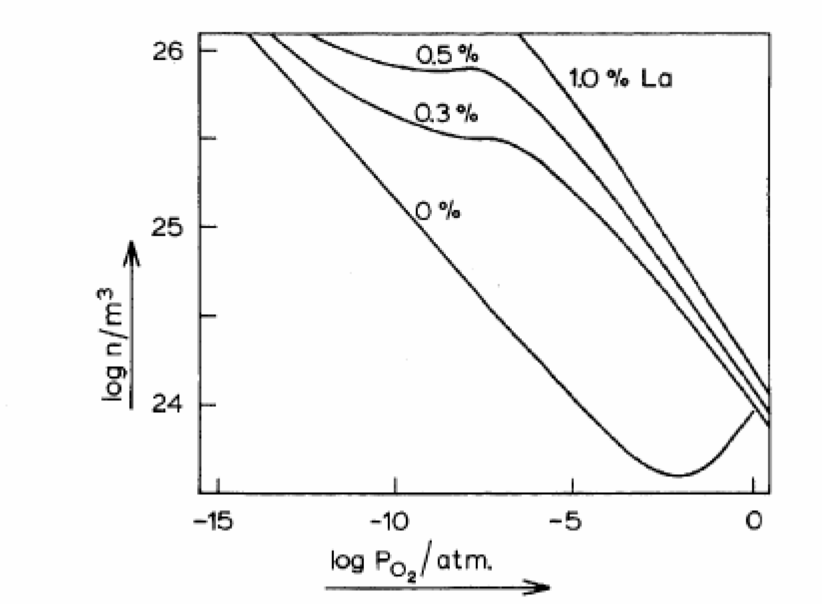


Figure 2.6. Equilibrium electron concentrations as a function of the oxygen partial pressure at 1200°C in undoped $BaTiO_3$ and doped $BaTiO_3$ with various La concentrations [40].

The electro neutrality equation form the observation is as follows: [40]

$$n + [V_{Ba}'] + 2\,[V_{Ba}''] \;=\; p + [V_O^{\bullet}] + 2\,[V_O^{\bullet\bullet}] + [La^{\bullet}] \qquad (2.3)$$

Where n – the concentration of conduction electrons

p- concentration of holes

$[La^{\bullet}]$ - the concentration of La atoms substituted at Ba site and ionized

As stated earlier trivalent lanthanum (La^{3+}) replaces divalent barium (Ba^{2+}) on the A-site in the perovskite ABO_3 structure and is too large to replace Ti on the B-site.

Due to the extra positive charges in the foreign ions, charge imbalance is created which must be compensated by either cation vacancies on the A- or B-site (ionic compensation), or by electrons (electronic compensation). As the La concentration increases, there is an initial drop in resistivity, and is generally attributed to electronic compensation of the substituted cation via "donor-doping".

The chemical composition of the materials has the general formula, $Ba_{(1-x)}La_xTiO_3$ where x is the donor dopant concentration. The effect of donor concentration on room temperature conductivity is negligible at x >0.5 atm % which is due to immobility of cation vacancies. The subsequent rise in electrical resistivity is commonly attributed to a change in doping mechanism to ionic compensation via the creation of cation vacancies [53], where the compensating defects are Ti vacancies with the general formula $Ba_{(1-y)}La_yTi_{(1-y/4)}O_3$. Ionic, electronic compensation mechanisms are represented by equations (2.4) and (2.5) respectively. These defects can be represented using Kroger–Vink notation, with atoms represented by their normal chemical symbol and vacancies by the symbol V. Subscripts indicate atom normally occupying the vacant site, thus V_{Ba} is a vacancy at Ba site. Interstitial site (A_i) is indicated by a subscript i, electron and holes are represented by (e), (h) respectively.

Like normal atoms, defects will also have charges and it is useful to distinguish actual charges from effective charges. Actual charges are present inside the bounds of the defect, where as effective charges are the difference between the actual charge at the A site and the charge normally present at that site if no defect is present.

For interstitials, the actual and effective charges are the same and for substitutional atoms or vacancies the two are different [46]. The effective charges are represented by superscripts + and -, effective charges by dots (•) and primes (') and an effective charge zero is indicated by superscript (x).

According to F.D.Morrison *et al.* [54], the possible compensation mechanisms is given by the following: Ionic compensation mechanism and the electronic compensation mechanism

$$4Ba^{2+} + Ti^{4+} \longrightarrow 4La^{3+} + V_{Ti} \qquad (2.4)$$

$$Ba^{2+} \longrightarrow 2La^{3+} + V_{Ba} \qquad (2.5)$$

$$Ba^{2+} \longrightarrow La^{3+} + e^{-}$$

(2.6)

These may be written in Kroger–Vink notation as: Ionic compensation mechanism and the electronic compensation mechanism

$$4Ba^{x}_{Ba} + Ti^{x}_{Ti} \longrightarrow 4La^{\bullet}_{Ba} + V''''_{Ti} \qquad (2.7)$$

$$3\,Ba^{x}_{Ba} \longrightarrow 2\,La^{\bullet}_{Ba} + V''_{Ba} \qquad (2.8)$$

$$Ba^{x}_{Ba} \longrightarrow La^{\bullet}_{Ba} + e' \qquad (2.9)$$

From equation (2.4), incorporation of lanthanum (La^{+3}) into $BaTiO_3$ occurs entirely at titanium vacancies [48]. Negligible effect of ionic compensation on the room temperature conductivity is observed due to the immobility of cation vacancies from equations (2.4), (2.5), where compensation effect of La doped $BaTiO_3$ will remain insulating.

In contrast electronic compensation from equation (2.6), will cause a substantial increase in conductivity where the number of carriers is equal to the La concentration [54].

Similarly, the defect reactions mentioned earlier in term of the Kroger–Vink notations are as follows [54]:

$$2\,La_2O_3 + 3\,TiO_2 \longrightarrow 4La^{\bullet}_{Ba} + 3\,Ti^{x}_{Ti} + 12\,O^{x}_{O} + V''''_{Ti} \qquad (2.10)$$

$$La_2O_3 + 3\,TiO_2 \longrightarrow 2La^{\bullet}_{Ba} + 3\,Ti^{x}_{Ti} + 9\,O^{x}_{O} + V''_{Ba} \qquad (2.11)$$

$$La_2O_3 + 2TiO_2 \longrightarrow 2La^{\bullet}_{Ba} + 2\,Ti^{x}_{Ti} + 6O^{x}_{O} + \tfrac{1}{2}\,O_2 + 2\,e' \qquad (2.12)$$

If the electrons are primarily associated with Ti then the equation (2.12) can be written as follows:

$$La_2O_3 + 2TiO_2 \longrightarrow 2La^{\bullet}_{Ba} + 2\,Ti'_{Ti} + 6O^{x}_{O} + \tfrac{1}{2}\,O_2 \qquad (2.13)$$

In addition to the donor doping mechanism, there is a second mechanism by which semiconductivity occurs and is associated with the loss of oxygen during heating at high temperature or at low partial pressure of oxygen [55].

$$O^{2-} \longrightarrow \tfrac{1}{2} O_2 + 2e^{-} \qquad (2.14)$$

Oxygen loss in La doped ceramics during heating at 1450°C in air [54, 56], is partly reversible on cooling to give electrically heterogeneous ceramics that have resistive grain boundaries and/or surface layers. But they have semiconductive grain cores, where reoxidation process appears and is responsible for resistivity anomaly in donor-doped $BaTiO_3$ [28]. Reduced in vacuum or in an inert atmosphere of donor doped $BaTiO_3$ samples resulted in the disappearance of resistivity jump, and will reappear with subsequent annealing in an oxygen or halogen atmosphere. When gas ions become chemisorbed at the grain boundaries, conduction electrons are also trapped at the interface [28,152].

At higher donor concentrations, semiconductivity is retained even when the reoxidation process is avoided. In an alternate process, in the presence of excess oxygen, all concentrations of La doped $BaTiO_3$ ceramics showed an insulating behavior [57]. Highly pure materials prepared by sol-gel route at moderately low sintering temperatures (~1100°C), sample of undoped and donor-doped $BaTiO_3$ are insulating and show no evidence of conducting cores and also no evidence of semiconductivity either with donor doping or oxygen loss [58]. In contradiction to the donor doping concept, a distinct PTCR effect with a core-shell structure was observed in undoped high-purity barium titanate ceramics heated at 1350°C in air [37, 59].

2.5 Effect of Donor, Acceptor Additives on Electrical Properties and Processing Characteristics

Ferro-electric polycrystalline ceramic $BaTiO_3$ when doped with trivalent (La^{3+}, Nd^{3+}, Sb^{3+}, Y^{3+}, Sm^{3+} etc.) or pentavalent (Nb^{+5}, Sb^{+5} etc.) ions will show abnormal positive temperature coefficient of resistance. Donor doped polycrystalline $BaTiO_3$ ceramics sintered in air or oxidizing atmosphere exhibit an anomalous increase in electrical resistivity during tetragonal to cubic phase transition at Curie temperature ($T_c \sim 120^0C$) [4,8,27,60-64].

Interesting changes can be observed with partial substitution of A site ion with suitable impurities. Multiple ion occupation of A and/or B site in ABO_3 compound is expected to bring changes in Curie temperature and other physical properties [63]. In general either IIIrd group or Vth group elements are used as dopants. Doping with a number of rare earth oxides dopants and as well as, a number of transition 3d acceptor elements cause barium titanate to form an n-type semi-conducting with a resistivity of about $10\text{-}10^2$ Ω-cm [65, 66]. Doping should be made either at Ba site or Ti site. Besides cation donors, some anions can serve as donors in $BaTiO_3$ [29].

PTCR behavior is also observed in acceptor (Mn) doped $BaTiO_3$ which is an insulator at room temperature. Minimum PTCR effect is observed for samples sintered in the presence of forming gas (N_2 and 0.2 % H_2) is maximum in samples sintered in CO/CO_2 mixture [67].

The PTCR effect is enhanced considerably by annealing in nitrogen atmosphere. Again restoration of insulating behavior is observed at higher dopant concentrations. Such type of conductivity anomaly is believed to be either due to grain size effect arising from kinetic process during heating and cooling [68], or due to change in mode of donor compensation from electrons to cation vacancies [89]. The formation of solid solutions of $BaTiO_3$ during with various materials have been studied doping on their properties of $BaTiO_3$ were also studied [70-73]. Most of these studies involved replacement of barium ions by other divalent cations (aliovalent) such as Ca^{+2},Sr^{+2},Pb^{+2} and Ti^{+4} ions by Zr^{+4} and Sn^{+4}.

Small amount of Ca^{+2} substitutions will improve the low temperature resistance aging behaviour [71], as well as improve the grain size and microstructure of PTCR ceramics [72]. Considerable rise in magnitude of the resistance is observed either by doping with acceptor dopant or by annealing below sintering temperature. A Significant change in Curie temperature is also made by partially substituting for Ba^{+2} either by adding with isovalent Sr^{+2} or Pb^{+2} in the temperature range of -80°C to 360°C [73]. Experimental results by Harman [22] indicate that with small changes in the percentage of samarium (Sm^{+3}), there is considerable change in the electrical resistivity values observed in all temperature regions.

Saburi [13, 14] has studied the effect of cations of higher valence as well as of lower valence than that of Ba^{+2} or Ti^{+4}. Higher valence cations (Bi, Ce, La, Nb, Nd, Pr, Sb, Sm, Ta), at 0.3 molecular percent considerably reduce the room temperature resistance, and imparts anomalous PTCR characteristics. Where as on the other hand the same concentrations of lower valence cations (Ag, Co, Ga, Mn, V, W, Zn) results in considerably high room temperature resistance with no PTCR effect.

In general there are 3 types of additive added in the preparation of PTCR ceramics: (1) donor dopant additives (2) acceptor dopant additives (3) sintering aids for property modification. As the concentration of the donor dopant increases, electrical resistivity increases up to a certain point and then decreases gradually. Semiconducting behaviour reverts to insulating with excess donor dopant concentration. Concentration limits of the donor dopants vary from dopant to dopant, with considerable changes in the entire properties of the material.

The Conductivity and Curie point of PTCR ceramics developed at a narrow range of dopant concentrations. Figure 2.7, shows the conductivity and Curie point of $BaTiO_3$ as a function of Sb_2O_3 at room temperature, where higher concentrations the material becomes insulating. Due to poor sinter ability, pure $PbTiO_3$ has a low potential as a ferroelectric material. Where as $PbTiO_3$ doped with MnO_2 showed maximum resistivity even in the atmosphere of nitrogen. The electrical resistivity of the MnO_2 doped specimens averaged 1000 times grater than that of specimens with other additives [74], and also results in high mechanical strength and a small dissipation factor.

A small quantity of donor ions in conventional air firing produces discoloration, semiconductivity and grain sizes of > 10 μm [75]. Moderate sintering temperatures allow the preparation of small grained in conjunction with reduced oxygen partial pressure [75] with Nb concentrations <= 0.35 at. %. The effect of dopants on the catalytic activity and work function were examined by Mikhailava *et al.* [76], where the decrease in the work function for La doped $BaTiO_3$ decreases the catalytic activity.

Characterizing surface states and the catalytic activity of semiconducting $BaTiO_3$ was examined by oxidation of CO on La_2O_3 [77]. Increase in conductivity with a linear increase in concentration of rare earth doped single crystal $BaTiO_3$ is observed by Murakami *et al.* [78].

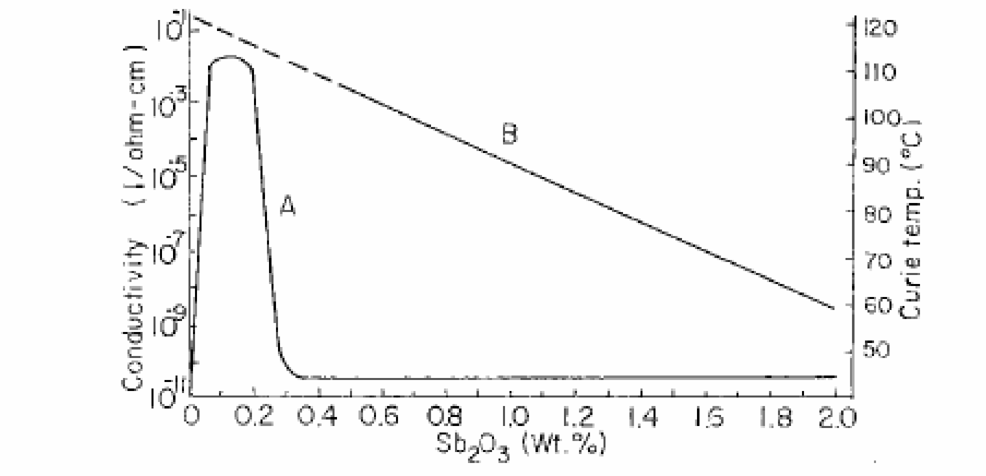


Figure 2.7. Conductivity (A) and Curie point, (B) of $BaTiO_3$ as a function of the Sb_2O_3 impurity at room temperature [79].

La^{+3} has almost same atomic radii as that of Ba^{+2} and will substitute on the barium site resulting in an n-type semiconducting in the narrow concentration range, where as atomic radii of Y^{+3} is in between Ba^{+2} and Ti^{+4} and can substitute on either site and can act as both donor and acceptor [73]. Yttrium oxide (Y_2O_3) can act more as an acceptor dopant in the presence of excess Ba and as a donor in the presence of excess Ti [80]. Yttrium is only partly incorporated into grains as a result of rapid grain growth, while the rest of it remains in intergranular phase [81].

The coordination number of Y^{+3} is 7 which is close to the coordination number of Ti ion in the perovskite which is 6, occupies the Ti site preferably when $BaTiO_3$ was doped at low sintering temperatures.

Y_2O_3 doped $BaTiO_3$, when sintered at low temperature is represented by the following equation: [82]

$$Y_2O_3 \longrightarrow 2\,Y'_{Ti} + 3O^{x}_{O} + V^{\bullet\bullet} \qquad \textbf{(2.15)}$$

Qi Jainquan *et al.*, also reported that yttrium doped into $BaTiO_3$ results in the increase of oxygen vacancy and promotes grain growth. Acceptor, Er^{3+} is forced into either barium or titanium sub-lattice analogous to that of donor Y^{+3} [68]. As the concentration of donor dopants increases, grain growth is inhibited, with increased barium vacancies, and increase in electrical resistivity [80, 83]. Rare-earth oxides such as Gd_2O_3 and Dy_2O_3 inhibit the grain growth in $BaTiO_3$ ceramics [84].

From the results of Kahn [75], larger grains were produced when $BaTiO_3$ doped with < = 0.35 atm.% Nb is sintered in air. Beyond this concentration (~>= 0.4 at %) only grains of <= 1μm size were reported. However sintering in CO atmosphere at higher temperatures produced larger grains > 1μm size. From these, observation, not only the concentration effects the grain growth, but also the sintering schedule and sintering atmosphere. From Desu and Payne, this grain growth inhibition is due to grain boundary segregation [85].

Kahn also reported [86], that the dielectric constant of small grained material is higher than that of the large grained ceramics. Spontaneous internal stresses are developed in the ferroelectric barium titanate with small grain size, which also enhances the dielectric properties of the material, and whose orthorhombic-tetragonal phase transition is influenced more by the grain size, rather than their tetragonal-cubic phase transition [87].

Addition of rare-earth oxides also alters the lattice constant values, because of the difference between the ionic radii of the trivalent rare earth ions and those of Ba^{+2} and Ti^{+4} [88]. A limited amount of rare-earth doping (La^{+3}) into $BaTiO_3$ results in the introduction of Ba-site vacancies and as well as Ti-site vacancies [89]. Existence of barium vacancies greatly alters the chemical bonding, in the host lattice, which causes some loss of oxygen which leading to the formation of oxygen vacancies at elevated temperatures. This again makes the material semiconductivity.

Al-Allak [118,119] presented a new PTCR model in the presence of Mn acceptor, where the dominating defects within the depletion layer are Mn ions with compensating oxygen vacancies. Basu *et al.* [91], reported that antimony (Sb) doped $BaTiO_3$ with slightly excess Ti sintered at 1350°C, showed an increased room temperature resistivity with increasing sintering time. They also made interesting observation that there is almost 4 orders of increase in PTCR effect even with zero sintering time. This is in contrast from the early days of the PTCR research which has reported that long sintering time (20-30 hours) at high sintering temperature ~1350°C is necessary to diffuse the impurity throughout the specimen [22].

As the research on the PTCR ceramics advances in the past years sintering time has been considerably reduced with improved properties. The amount of lanthanum dissolution can be determined by measurement of T_c change, using differential thermal analysis (DTA) [92]. Several attempts have been made to enhance the of PTCR property of ceramics. In one process, addition of manganese oxide improves the PTCR property of $BaTiO_3$ doped with rare earth Bi or Sb [93]. Earlier no attempts were made with combined mixture of Nb_2O_5 and MnO_2, since the formation of $MnNb_2O_6$ might disturb the PTCR behavior, while Matsuoka *et al.* [94] reported that increased concentrations of both MnO_2 and Nb_2O_5 improved PTCR behavior greatly.

Manganese influences both the electrical properties and as well as microstructure by acting as an effective acceptor dopant and is especially used in fabricating capacitors and PTCR devices. Initially it was thought that the existence of transition metals such as Fe or Mn [95] in semiconducting $BaTiO_3$ is detrimental its semiconductivity and make the material insulating. By the addition of small amounts of some of the 3d-transition metal ions to semiconducting $BaTiO_3$, then it will be substituted for Ti^{+4}, which will act as an acceptor impurity enhance the PTC resistivity jump.

Although this behavior has been modeled by Daniels *et al.*, [96] they tried to explain the exact difference between the acceptor levels in 3-d transition elements to that of non acceptor doped PTCR ceramics in their model. Ueoka *et al.* [97] examined the electrical behavior of barium titanate using the first row of transition metals and succeeded in manufacturing high performance PTCR thermistors.

This is especially true for Manganese ion doped materials which exhibited tremendous enhancement in resistivity values with high durability at high voltages. Research have also indicated, adding additives including sintering aids and certain ions can affect the PTCR behavior of ceramics as shown in figure 2.8. This figure illustrates the pronounced and scarcely pronounced, resistivity-temperature characteristics of Nd-doped $BaTiO_3$ with different additives.

Ueoka [98] also proposed a model for the case of acceptor (Mn), and is also valid for other transition metal ions. During sintering manganese is present as Mn^{+2} on the titanium site and is compensated by doubly ionized by oxygen vacancies. During the cooling stage, the oxidized grain boundaries change the oxidation state of Mn^{+2} to Mn^{+3} or Mn^{+4} with higher acceptor levels. Reversible changes in oxidation states with magnetic susceptibility measurements, when samples annealed with different partial pressures of oxygen's were identified by Hagemann *et al.* [99,100], and were only applicable to a few transition elements like Mn, Cr, Co.

In donor doped PTCR ceramics, Mn depresses the grain size and enhances the electrical resistivity properties [101]. Also abrupt changes in the crystallographic structures between 1.5 and 1.8 mol% of Mn were observed. On the contrary , Kurata and Kuwabara [102], reported that grain size of the La doped $BaTiO_3$ considerably increased up to tens of micrometers with increasing Mn concentration up to 0.08 mol% accompanied by maximum resistivity jump.

Beyond this concentration, an abrupt grain growth anomaly is observed. From differential reflectance and electrons spin resonance spectroscopy (ESR) [103], the room temperature resistance of the combined La and Mn doped $BaTiO_3$ samples sintered in air was lower than that of La doped samples alone. The grain growth is also promoted with Mn addition. It is also known from the research of Hagemann [104] that doping with transitional metal ions affects the hysteresis loop and dielectric loss properties of the ferroelectric materials. Also the valence states of the doped 3d-transition metal ions were determined by magnetic-susceptibility measurements. As stated earlier, Mn ions can change their valence states depending on the atmosphere, from tetravalent (Ti^{+4}) at the region of higher oxygen partial pressure (P_{O2}) to divalent (Mn^{+2}) or trivalent (Mn^{+3}) at low oxygen partial pressure region [100,104]. The decrease of PTCR effect in La-Mn co-doped samples sintered in air was reported and assumed to be due to the chemisorbed oxygen at the grain boundary region, where a valence change of Mn^{+3} to Mn^{+2} [103].

Peng *et al.* [105, 106] have studied the effect of both Mg-La, Mn-La doped $BaTiO_3$, where both Mg, Mn acceptors will compensate for lanthanum with different doping mechanism. The Mg will incorporate into the body of grain, can only exist in the grain boundaries [105,106].

In general donor dopants were added before the synthesis of $BaTiO_3$. However, Qi Jainquan *et al.* have reported [107], adding small amount of donor dopant during the sintering process along with acceptor dopants. At high temperatures some oxides are highly volatile that are loss during sintering and can cause compositional changes that greatly influence the properties of the sintered bodies [108].

When $Ba_{(1-x)}SrTiO3$ is doped with Bi_2O_3 vapour during the sintering , the magnitude of the resistivity jump and the PTCR is increased, while the grain growth is suppressed [109]. The magnitude of resistivity jump is further enhanced when it is co-doped with manganese to form a more stable composite trap center [110].

Vapor phase doping, either with MnO or Sb_2O_3 during synthesis was studied by Suman Chatterjee *et al.* [111]. Vapour phase doping results in preferential distribution of acceptor ions at the grain boundaries resulting in improved PTCR characteristics to produce high performance sensing PTCR Thermistors. M.Mahesh Kumar *et al.* [112] have tried, to synthesize materials with both PTCR and relaxation effects by double doping $BaTiO_3$ with Bi^{+3} and Fe^{+3} on A and B sites of ABO_3 perovskite. However the materials does not yield PTCR characteristic, but gave a relaxor behavior.

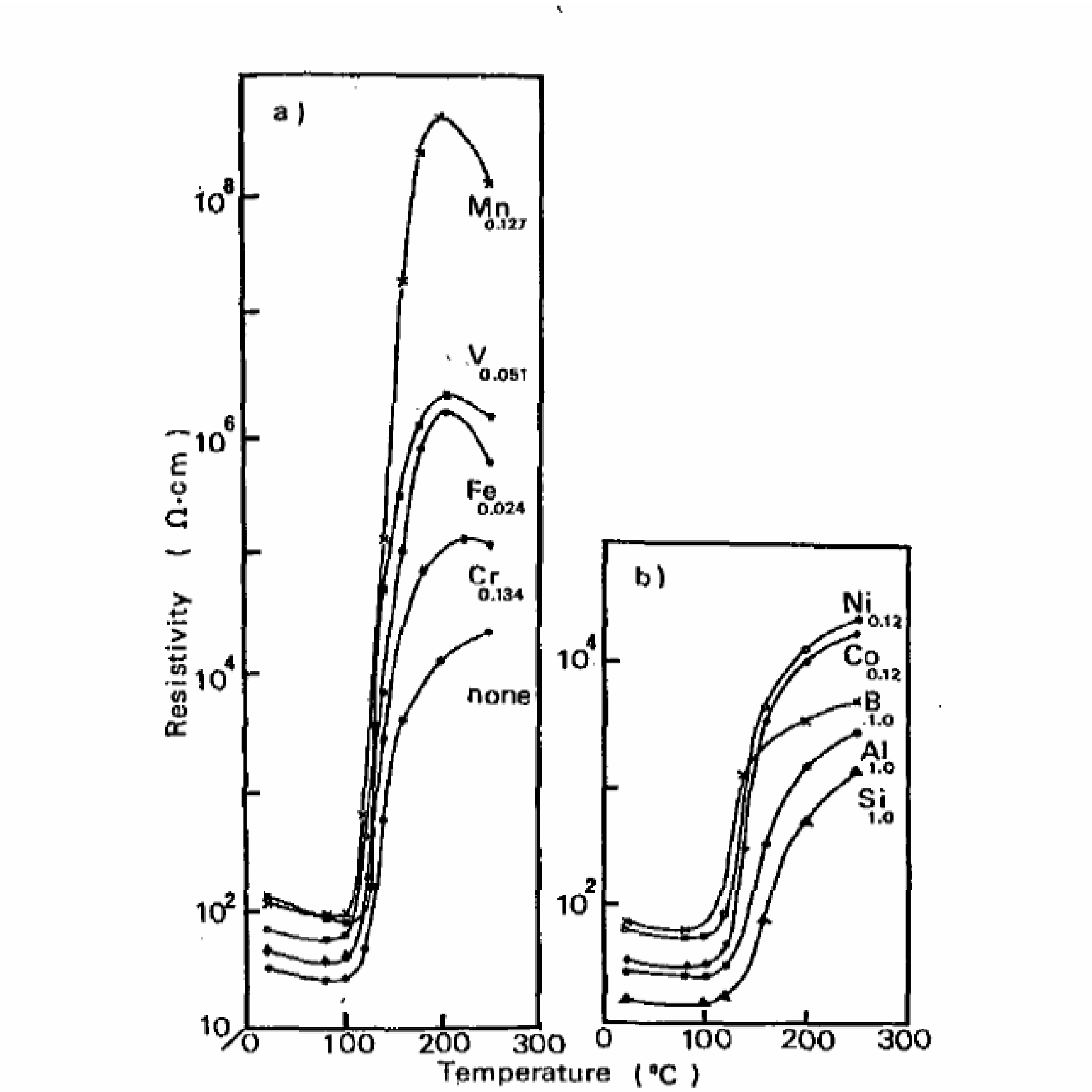


Figure 2.8. Resistivity-Temperature characteristics of Nd-Doped $BaTiO_3$ ceramics containing various additives [97].

2.6 Effect of Sintering Aids and Processing Characteristics

Processing conditions such as sintering temperature, soaking time, sintering atmosphere, and cooling greatly effects the properties of PTCR ceramics. Making use of highly pure raw materials is a necessary condition in producing PTCR sensors with good properties. For preparing $BaTiO_3$ sensors, raw materials less than 99.4% purity is not recommended.

However impurities are always present in the raw materials, especially for those used for industrial ceramic manufacturing. Wet milling is the process which is commonly employed in barium titanate ceramic preparation [113] and is where most impurities come from. Source of impurities are from milling media such as water, grinding balls.

To minimize the impurities, it is desirable to use deionized water to avoid unexpected troubles. Jonker *et al.* [114] also reported that milling calcined oxides will also lead to additional contamination. In general ceramic samples sintered at low sintering temperature, results in an incomplete impurity diffusion and grain growth. Grain growth with high deviations in grain size and with low density indicating that solid state sintering is the dominant mechanism. An increase in sintering temperature results in uniform grain size and material densification by removing pores in the ceramic body. Beyond ~1350°C sintering temperature, densification decreases. The eutectic temperature of stoichiometric $BaTiO_3$ is ~ 1332°C, while as that of non-stoichiometric $BaTiO_3$ is in the range ~ 1280°C – 1350°C, depending on the stoichiometric ratios [115,116]. The necessity of the liquid phase formation in PTCR barium titanate has been recognized since the beginning PTCR technology.

The liquid phase segregates to the grain boundaries during sintering. Since the PTCR effect is a grain boundary phenomena, the formation of the liquid phase would be expected to be important in development of grain boundary acceptors and the PTCR behavior [19].

Common additives employed in the manufacture of PTCR ceramics include TiO_2, SiO_2, and Al_2O_3 [16, 34, 117]. These additives promote eutectic reactions with $BaTiO_3$ and form liquid phases when sintered. Combined mixture of Al_2O_3, SiO_2 and TiO_2 is generally called AST. AST in the molar ratio 4:9:3 is reported to be able to lower the room temperature resistivity considerably and improve the PTCR effect [117,118].

A small amount of silicates promotes the sintering of ceramics and are called mineralizers, and the voltage dependency of the semiconducting ceramics is greatly influenced by adding such type of mineralizers [34]. Matsuo *et al.* [117] reported that the addition of AST (Al_2O_3, SiO_2, and TiO_2) to industrial grade $BaTiO_3$ promotes the conductivity, unlike conventional additives such as La_2O_3 and Bi_2O_3. These additives will cancel the poisoning action of the natural impurities that are present in the industrial grade raw materials and results in semiconducting behavior with low resistivity values.

Matsuo *et al.* [117] also reported that resistivity of the $BaTiO_3$ ceramics decreased with addition of SiO_2 concentrations. The additive free $BaTiO_3$ ceramics had a resistivity greater than 10^{11} ohm-cm with a major impurity of TiO_2. This is lowered to around 10^3 ohm-cm, where as with the addition of 2 mol% of SiO_2. This is further lowered to 10 ohm-cm when 0.6 mol% of Al_2O_3 is added together with 2 mol% of SiO_2, where as the lowered resistivity values for $BaTiO_3$ with Al_2O_3 alone are around 4 orders of magnitude.

This rise in room temperature resistivity is possibly arises due to the formation of incompletely compensated surface states [4,119,120] caused by the segregation of aluminum ion at the grain boundaries [121].

In order to create a liquid phase during sintering and to reduce sintering temperature SiO_2 and excess Ti are added [122]. In general the eutectic temperature reduced from 1320°C of TO 1260°C [123] when excess Ti is added. H.F.Cheng reported [124] the existence of suitable amount of liquid phase is due to addition of SiO_2 and TiO_2 additives. These enhance the ionic diffusion and results in uniform microstructure of large grains of the ceramics. Excess amount of liquid phase will lead to formation of clusters with small particles which grow into large grains. Addition of Al_2O_3 will retard the grain growth. Cheng *et al.* [125], in another experiment reported that the quantity of liquid phase formed due to eutectic reaction between barium strontium titanate and AST is the prime factor in determining the grain size. Small grained high PTCR materials with low resistivity values and polaron deficient zones were prepared by Gaosheng Liu *et al.* [126], using excess Ba and small amount of SiO_2. They have also observed that the directional alignment of the domain structure through each grain which is indicative of the well dispersed donor dopant in the $BaTiO_3$ ceramics. This also indicates a transition from high resistive insulating behavior to low resistive semiconducting PTCR behavior. AST functions as an electron trapping agent and will induce Schottky potential barriers with increasing temperature coefficient values [127]. However this rule is only valid with increasing concentrations of acceptor densities combined with excess amount of AST in the range of 5-12 mol%.

An increase in maximum PTCR jump, with increasing AST concentrations were reported by Zhi Cheng Li *et al.* [128]. Their work indicated that microstructure observations revealed that re-crystallization takes place in crystals with low or no AST concentrations resulting in the loss of PTCR effect.

N.S.Hari *et al.*'s [129] experimental observations with different additives such as B_2O_3, SiO_2, Al_2O_3 reveals that the segregation of secondary phases ($BaAl_6TiO_{12}$,$Ba_3Al_{10}TiO_{20}$, BaB_6TiO_{12}, $BaTiSi_3O_9$) occurs at grain boundaries. The addition of Al_2O_3 broadens the PTCR curves, while a steep raise in PTCR jump is observed with B_2O_3 addition; there was not much broadening with SiO_2, even compared with that of donor doped samples.

A very low capacitance values measured by Gerthsen and Hoffmann [33], on single grain boundaries suggest that an intermediate layer of a Ti rich second phase exists at the grain boundaries. TEM results of Hannstra *et al.* [135] showed the presence of amorphous second phase at the contact of three or more grains and absence of any second phase in the grain boundaries. Recent results of Bamlai *et al.* [130] show that the grain growth was suppressed with TiO_2 alone. However the combination of TiO_2 and SiO_2 promotes liquid phase sintering, reduction in sintering temperature from ~1350°C to ~1250°C and enhanced the PTCR effect.

In order to further reduce the sintering temperature of PTCR ceramics, researchers have tried using Boron Nitride (BN) as sintering aid. Semiconducting $BaTiO_3$ ceramics have been prepared by Chyuan.Ho *et al.* [131] using BN as a sintering aid.

Addition of BN considerably reduced the sintering temperature to ~ 1100°C, a 200°C reduction from the normal sintering temperature. They also observed an enhancement of PTCR effect, due to the presence of boron (B) at grain boundary. It also promotes the grain boundary surface state density (acceptor-type state) after sintering with negligible incorporation of B at perovskite structure.

A Four component system (Ba, Sr, Ca, Pb) TiO_3 with BN as sintering aid is used by Huang *et al.* [132], to reduce the sintering temperature as well the room temperature resistivity. Huang *et al.* also reported elsewhere that [133], the performance of PTCR ceramics is not sensitive to sintering parameters such as sintering aids, cooling rate, and is recognized due to excess amount of BaO and low sintering temperature, there by eliminating the effect of Ba ion vacancies on the PTCR properties.

Where as increasing orders of PTCR with excess amount of BaO was reported by Miha Drofenik *et al.* They also observed anomalous grain growth (AGG) [150], due to the release of oxygen. $TiCl_3$ solution also influences the room temperature electrical properties and will inhibit the grain growth, by segregating the Ti^{+3} ions at the grain boundaries, by behaving as an acceptor dopants or by varying the valence from Ti^{+3} to Ti^{+4}, which will increase the surface charge density as well as the barrier height at the grain boundaries with which PTCR effect also increased [134]. Addition of YB_6 as sintering aid reduced the room temperature resistivity values by enhancing the densification of semiconducting $BaTiO_3$ by lowering the sintering temperature [155].

2.7 Heywang Model

Various theoretical and experimental models have been proposed to explain the PTCR effect in semiconducting $BaTiO_3$. From theoretical models studied on PTCR phenomena, Saburi [13,14], Heywang [27,79], Jonker [28,141,152] and Peria [153], In which most accepted models include, the Heywang model [27], based on grain boundary potential barrier model in interpreting the grain boundary mechanism of the phenomena and Jonker model [28], based on the influence of ferroelectric polarization on resistivity below the Curie temperature, T_c. These models were further extended by Daniels *et al.* [3], in terms of potential barrier layers formed at grain boundaries due to the presence of barium vacancies at the grain surfaces.

The PTCR effect in an n-type semiconducting $BaTiO_3$ was originally explained by Heywang in terms of temperature dependent, Schottky type potential barriers at the grain boundaries. Due to the fact that only n-type conductivity exists in $BaTiO_3$, blocking layers cannot be formed in bulk materials. However the surfaces or blocking layers are decisive in many experiments. Heywang observed two types of barrier layers which include, surface barriers existing at metal contacts appears from the possibility of getting high permittivity capacitive layers on reduced $BaTiO_3$ and interface or heterojunction barriers. Owing to acceptor states at the interface, a space charge layer is formed at the surface of $BaTiO_3$ grains. The majority charge carriers, electrons in the case of donor doped $BaTiO_3$ are trapped by acceptors states in the grain boundary region.

Conduction electrons trapped at the grain boundaries by acceptor states create a negatively charged grain boundary with a positively charged space charge region adjacent to the boundaries. There will be a bending of the conduction band and potential barrier (Φ_{bh}) at the grain boundary as shown in the figure 2.9.

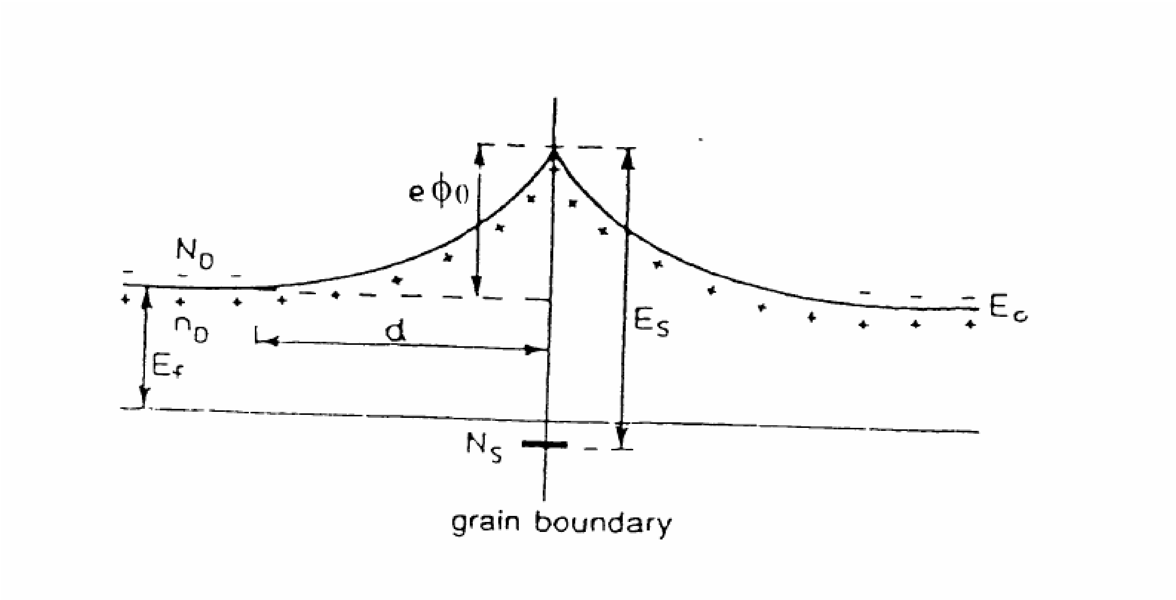


Figure 2.9. Space charge layer formed at the surface of $BaTiO_3$ grains [27].

The resistivity above the Curie temperature depends exponentially on the potential barrier (Φ_{bh}) in the grain boundary region and is given by equation (2.16).

$$\rho = \gamma \rho_g \exp (e \Phi_{bh}/k_B T) \qquad (2.16)$$

Where, e is the electron charge

k_B – The Boltzmann Constant

T – Temperature

ρ_g- Grain resistivity

γ- Geometric factor

According to The Heywang model, the potential barrier height is given by

$$\Phi_{bh}(T) \;= e\, N^2_e / (8\, \epsilon_0 \epsilon_{rgb}\, N) \qquad (2.17)$$

Where T is the absolute temperature, e the electronic charge, ϵ_0 the permittivity of free space, ϵ_{rgb} the relative permittivity of the $BaTiO_3$ within the grain boundary layer, N the donor concentration in the grain bulk, and N_e the temperature dependent concentration of the occupied acceptor states.

Where the charge neutrality condition is obtained by the relation between the grain boundary and the space charge region, the number of charge carriers trapped at the grain boundaries (N_e) will be related to the width of the space charge region (W_{scr}) and is given by

$$N_e = \;\; 2\, W_{scr}\, N \qquad (2.18)$$

Based on the Fermi-Dirac statistics, one can determine the concentration of occupied by the acceptor states (N_e)

$$N_e = \;\; N_s/(1+\exp(E_F + \;\Phi_{bh}(T) - \;E_S)/k_B\, T) \qquad (2.19)$$

Where $E_F = k_B T\, .\ln(N_c/N)$, Ns the density of acceptor states, E_s the energy of surface state in relation to the bottom of the conduction band, k_B the Boltzmann constant, T the temperature, E_F the Fermi energy level and the conduction electrons and N_c is the effective density of states, equal to the number of Ti ions per m^3, $N_c = 1.56 \text{ X } 10^{22}\ cm^{-3}$.

There are few difficulties in explaining the Heywang model from literature including, various types of resistivity-temperature characteristics, which were explained with equation (2.16). There is also no definite experimental support regarding the assumption of surface acceptors states which is certainly required for PTCR [136]. The complex resistivity equation which was propose by Desu *et al.* [137], better accounts for the effects of donors and thermal processing conditions on the room temperature electrical properties and is given by equation (2.20).

$$\rho = \rho_g \Big[1 + (W_{scr}\ k_B T \,/\, 2\, e\, \Phi_{bh}) \ \ (\exp\,(e\, \Phi_{bh}/k_B T) \Big] + W_{gb}\ \rho_{gb} \,/\, w_g \qquad (2.20)$$

Chapter 3

Fabrication of PTCR ceramic sensor

3.1 Introduction

This chapter discusses the powder preparation and the measurement techniques used for characterizing positive temperature coefficient of resistance materials. These include X-ray diffraction (XRD), Scanning electron microscopy (SEM), Energy Dispersive Spectroscopy (EDS) and Impedance analysis of the lanthanum doped $BaTiO_3$ used in obtaining n-type semi-conducting sensor with PTCR behaviour. Calcination of mixed oxides method was used in the preparation where the starting materials were doped with oxide group softeners, hardeners and stabilizers were added to enhance PTCR behavior. To examine the effect of sintering on ceramic sensor materials two batches of sensors were fabricated by applying two different sintering temperatures.

In PTCR ceramic sensor material technology and for most commercial applications, it is recognized that the sensors must have a relatively low room temperature resistivity ($\sim 10^1$-10^2 ohm-cm) along with large change in resistivity in order to optimize properties and have commercial applications [73]. Such property is only obtained with proper composition and processing parameters. Concentration of the doping elements plays a very crucial role in the fabrication and also on the electrical properties of the materials.

Since the PTCR effect has traditionally been observed at doping levels of 0.2 through 0.5%, to examine the effect of sensor materials at different concentrations, different concentrations of lanthanum doped $BaTiO_3$ sensors materials were prepared as shown in the table 3.1 and table 3.2 respectively.

Reproducibility of PTCR sensor depends on the uniform distribution of the dopants, counter dopants (acceptor) and also on the liquid phase sintering aids such as SiO_2, excess amount of TiO_2, and mixture of AST etc. Minute particles of dopants that are less than 0.5 atm% are added to insulating $BaTiO_3$ to make it semiconducting. Even very small amount of counter dopants, less than 0.05 atm% are added to enhance the grain boundary oxidation [4, 5, 19, 27,122]. Donor doped $BaTiO_3$ exhibit semiconductivty at relatively low concentration ranges of dopants i.e. 0.3-0.5 atm. %, but its insulating property is restored at higher dopant concentrations.

3.2 Raw Materials

Two batches of samples were prepared in the synthesis of La_2O_3 doped $BaTiO_3$ for PTCR sensor applications, one at low sintering temperature and the other at higher sintering temperature. All the starting materials used in this study were reagent grade. The chemicals used in the solid state synthesis of La doped $BaTiO_3$ were pure $BaTiO_3$, TiO_2 (325 mesh grade, 99.9%), La_2O_3 (99+), SiO_2 (99.995%), Al_2O_3 (Standard grade), MnO_2 (99+), C_2H_5OH (HPLC grade) all from Sigma Aldrich Ltd. Calcination of mixed oxides (CMO) was used to prepare trivalent lanthanum (La^{3+}) doped barium titanate.

Used molar concentrations for obtaining n-type semi-conductive $BaTiO_3$ are listed in Table.3.1, Table.3.2. To distinguish the samples easily from one another they labeled respectively as BLT1, BLT2, BLT3,BLT4,BLT5 for first batch of samples, and were sintered at 1100°C and MBLT1,MBLT2,MBLT3 for second batch of samples, sintered at 1350°C. To examine electrical properties of ceramic sensors, different concentrations of donor dopants and counter dopants were used in the preparation.

Table 3.1. Concentration of First batch of sensor material for La doped $BaTiO_3$.

Name	Compound	(Ba+La)/Ti (Molar ratio)	La_2O_3 (Mol %)
BLT1	$Ba_{0.9995}La_{0.0005}TiO_3$	1	0.0005
BLT2	$Ba_{0.999}La_{0.001}TiO_3$	1	0.0010
BLT3	$Ba_{0.998}La_{0.002}TiO_3$	1	0.0020
BLT4	$Ba_{0.9975}La_{0.0025}TiO_3$	1	0.0025
BLT5	$Ba_{0.997}La_{0.003}TiO_3$	1	0.0030

Table 3.2. Different concentration of second batch of sensor materials for La doped $BaTiO_3$ with Acceptor MnO_2 and AST as sintering aid.

Name	Compound	(Ba+La/Ti) (Molar ratio)	La_2O_3 (Mol %)	MnO_2 (Mol %)	Al_2O_3 (Mol %)	SiO_2 (Mol%)	TiO_2 (Mol %)
MBLT1	$Ba_{0.9995}La_{0.0005}TiO_3$	1	0.0005	0.02	1.67	3.75	1.27
MBLT2	$Ba_{0.999}La_{0.001}TiO_3$	1	0.0010	0.04	1.67	3.75	1.27
MBLT3	$Ba_{0.997}La_{0.003}TiO_3$	1	0.0030	0.06	1.67	3.75	1.27

3.3 Sample Preparation

Flow charts for fabrication of the donor doped and acceptor co-doped $BaTiO_3$ ceramics are shown in the following figure 3.1, figure 3.2 respectively. Initially sensor materials were ground with agate mortar and pastel by wet method using ethyl alcohol for 1 hour. The first batch (BLT1, BLT2, BLT3, BLT4, and BLT5) and the second batch (MBLT1, MBLT2, and MBLT3) of mixed ceramic sensor materials were ball milled into fine powders in acetone medium for 15 hours. Intimately mixed powders were undergone calcination at 1100°C for 5 hours in box furnace using alumina-silicate crucible. Grounding process was again repeated for calcined samples with same specifications as for pre-calcined sensor materials.

The first batch of sample were prepared without any sintering aid and as well as PTCR enhancers. However the second batch of samples were mixed with different molar concentrations of counter dopant MnO_2 acceptor and a constant molar ratio (4:9:3) of AST mixture (Al_2O_3, SiO_2, TiO_2) as sintering aid. Organic binder in general called rehological agent, was avoided purposefully. Many pellets were prepared at different applied pressures to examine the effect of the sensor material characteristics with a maximum applied pressure of 100Mpa. Sensor materials were pressed into disc shaped pellets by applying pressure of 100MPa using the experimental setup shown in figure 3.3. The first batches of samples were sintered at 1100°C temperature for 2 hours in air using a Carbolite programmable furnace and allowed to cool in furnace itself. Secondary thermal treatment was performed on the first batch of samples at 400°C for 1hour. The second batch of samples were sintered at 1350°C using a Carbolite programmable furnace for 2 hours in air and then allowed to cool in furnace. Secondary thermal treatment was also performed on the second batch of samples at 400°C for 1hour. Lowering of sintering temperature with enhanced PTCR behavior is the ultimate goal in the present research. In this process two batch of samples studied, with slight variations in the sintering profiles. Sintering profiles for both batches of samples were shown in the figure 3.4, figure 3.5 respectively. To examine the overall densification and the homogeneous distribution of donor dopant, counter dopants and as well as sintering aid on the PTCR ceramic sensor , two different sintering temperatures profiles were considered for the present thesis. To achieve diffusion of oxygen into the grain boundaries a process called secondary thermal (annealing) treatment was preformed on both batches of samples for 1 hour at 400°C.

To achieve semi conducting behavior for sensor, dopants need to be distributed to grains, counter dopants need to be segregated into the grain boundary region and liquid phase sintering aids also need to be distributed thought the microstructure. The presence of liquid phase sintering aids in the grain boundary region also plays a vital role in the distribution of oxygen along the grain boundary region during secondary thermal treatment and cooling stage. During annealing the oxidation of Ti^{+3} to Ti^{+4} occurs at grain boundaries to make them insulating, the insulating nature of grain boundaries gives rise to potential barrier and the resistivity jump [19].

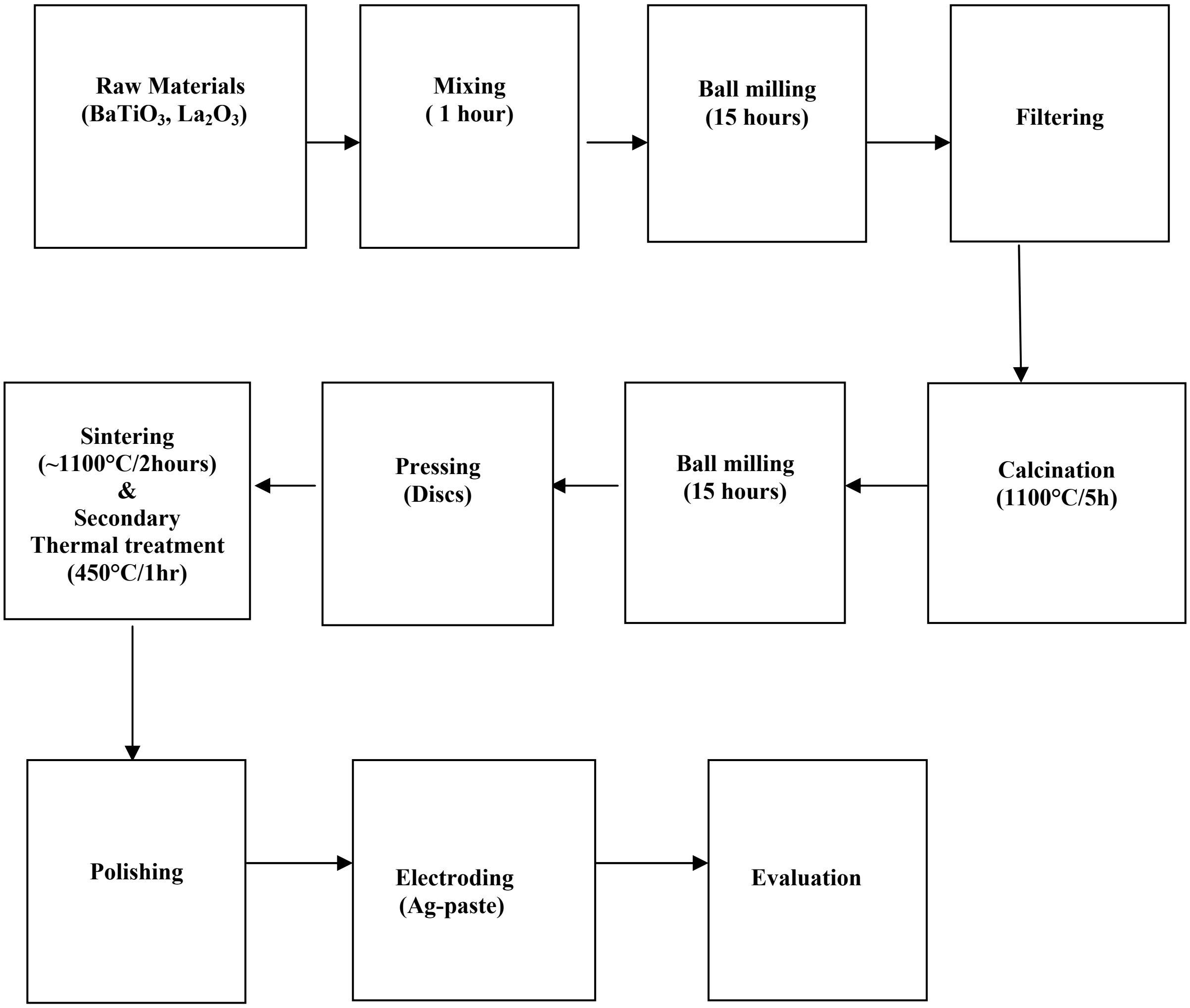


Figure 3.1. Preparation flow chart for BLT1-BLT5 of La$_2$O$_3$ doped BaTiO$_3$.

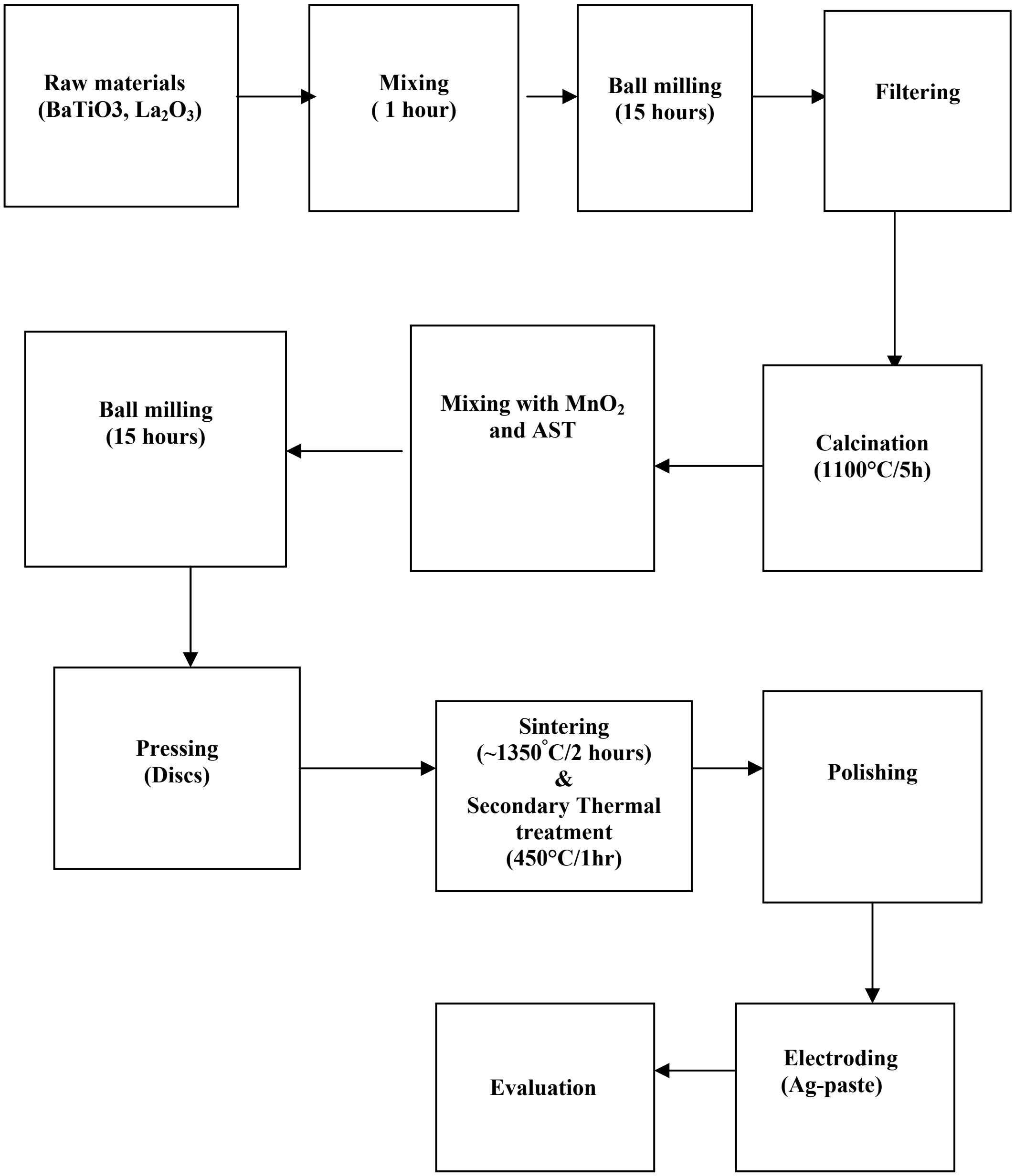


Figure 3.2. Preparation flow chart for MBLT1-MBLT3 of La_2O_3 doped $BaTiO_3$.

Figure 3.3. Experimental setup for pellet preparation of La doped $BaTiO_3$.

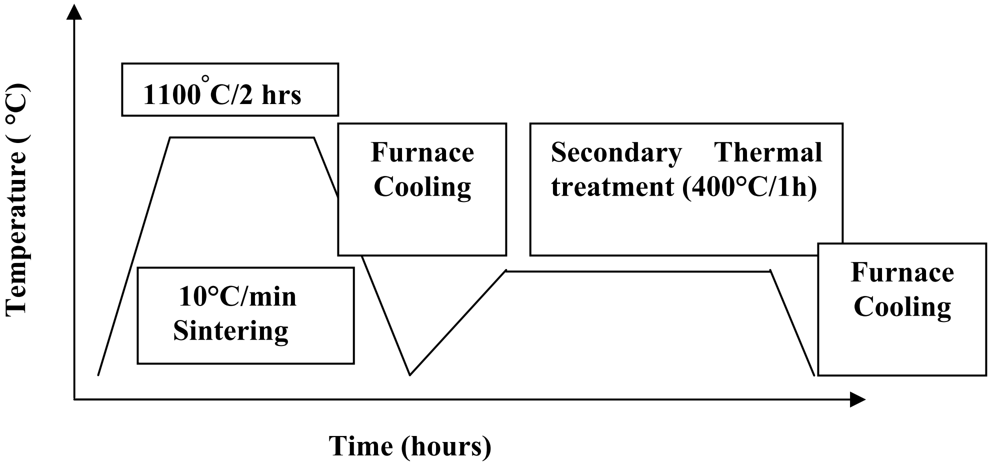


Figure 3.4. Sintering profile for BLT1-BLT5 sample followed in the preparation of n type semi-conducting $BaTiO_3$.

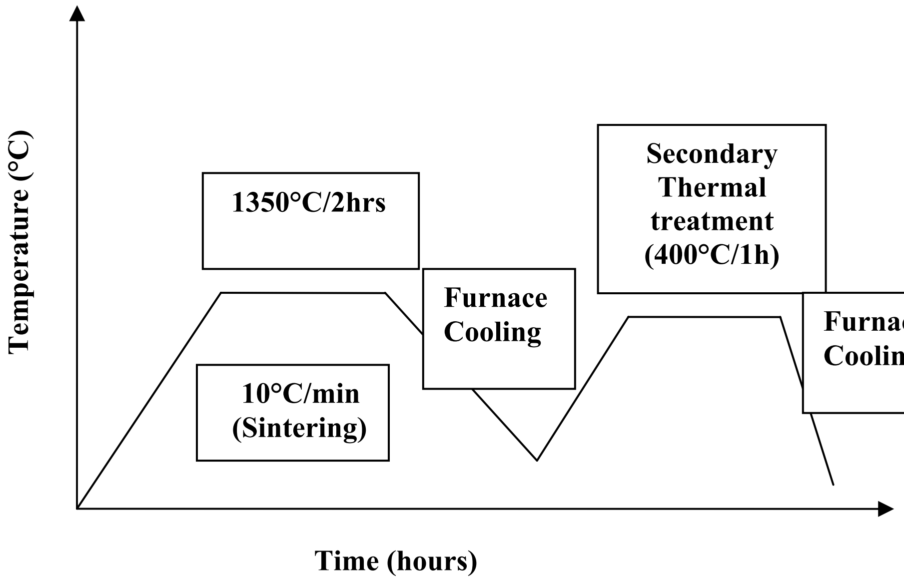


Figure 3.5. Sintering profile for MBLT1-MBLT3 sample followed in the preparation of n type semi-conducting $BaTiO_3$.

3.4 Structural Property Analysis

This section will discuss the various characterization techniques used in the fabrication of the lanthanum doped $BaTiO_3$ semi conducting ceramic sensor materials which include X-ray crystallographic analysis for phase identification, SEM analysis for microstructural analysis, to find the average grain size of the grain throughout the morphologies, densification and porosity. EDS analysis is also used to determine the elements that are present after the densification process.

3.4.1 Crystallographic Analysis (XRD analysis)

Perovskite family of crystals such as $CaTiO_3$, $BaTiO_3$, $PbTiO_3$, etc., with general formula ABO_3 has considerable interest for crystal physicists and materials engineers.

This is due to ferroelectric behaviour of these materials and structural phase transitions [138]. Below the Curie temperature (~120°C) $BaTiO_3$ is ferroelectric and show tetragonal structure with primitive space group P4/mmm (C^1_{4v}). However above this temperature it is taken a cubic structure with Fm3m (O^1_h) space group. $BaTiO_3$ undergoes a tetragonal-cubic transition at its Curie temperature. At low temperature $BaTiO_3$ crystal also undergo other structural transformation like orthorhombic at 5°C with primitive space group (Amm2) and rhombohedral symmetry (R3m) or trigonal at -90°C respectively. X-ray diffraction measurements for elemental analysis of the (structural properties of the) for both batches of the samples were carried out on intimately mixed Lanthanum oxide (La_2O_3) doped $BaTiO_3$ calcined for 5 hours at 1100°C, using D8 Advance Bruker X-ray Diffractometer with CuK_α radiation. XRD patterns were scanned in the 2-theta (2θ-degree) range of 20°-60° at room temperature.

3.4.2 SEM Characterization and EDS analysis

Microstructure changes were analyzed using scanning electron microscope (SEM). In general SEM analysis is used to observe morphologies of the sintered fractured surfaces, to determine the average grain size and to check the uniformity as well as the overall grain growth of sample. The energy dispersive spectrometer is an attractive tool for qualitative X-ray microanalysis, and is allowed to acquire rapid evaluation in a short time (~ 10-100 sec). Grain growth, microstructure changes in sensor material were analyzed using SEM analyzer and compositional variations were observed using Energy Dispersive X-Ray Spectroscopy (EDS) analysis.

SEM photographs, EDS results were taken for fractured specimens at different magnifications using Philps XL 30S FEG. Surfaces of the sintered pellets were smoothened with 600 # SiC paper and thermally etched and polished with 9µm diamond paste. A conductive Platinum coating was sputtered on sample and SEM photographs were taken at different magnifications at 5.0 kV. However when EDS peaks were measured, a 20 kV was applied. The Sintered samples were polished with No.600 SiC (silicon carbide) grinding paper and electrodes were deposited on either side of discs by silver epoxy paste for resistivity-temperature (ρ-T) characterization. The average grain size of the SEM micrographs was calculated using line intercept method using the following equation and inverse of L is called the average grain size.

$$\mathbf{L = (Ng/l) \ X \ M} \qquad \mathbf{(3.1)}$$

Where,

1/L – The average grain size

Ng (Number of grain boundaries crossing)

l- Length of the line (~10cm)

M- Magnification of the micrograph

3.5 Resistivity Measurements

Resistance-Temperature measurements were made by applying a constant dc voltage source (0.01 V_{dc}) by using a 4 point probe technique with a digital multimeter (Aligent–HP 34401A) in a temperature range from (room temperature) 20°C to ~200°C using a silicone oil bath and hot plate to heat the sample. Temperature readings were monitored with K type thermocouple with (HP 34970A) Data Acquisition/Switch unit as shown in the figure 3.6.

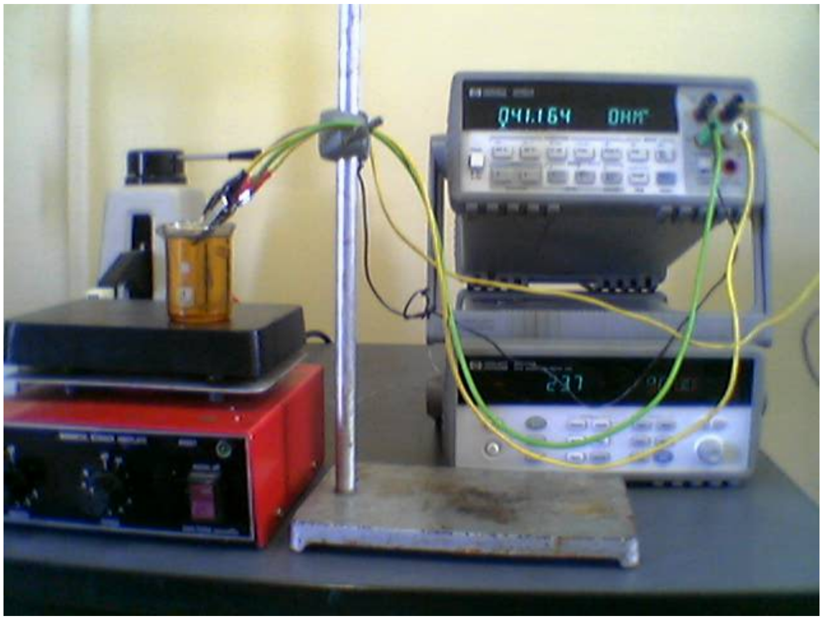


Figure 3.6. Equipment setup used in Resistivity-Temperature (ρ-T) measurements.

The thickness and diameter of the sintered samples were measured before electroding, in order to calculate the dielectric constant and resistivity from the measured capacitance and resistance values. Resistivity (ρ-ohm-cm) of the sintered pellets was measured from the dc resistance (R-ohm), length or thickness of the pellet l (cm) and the area of cross section of the pellet, A (cm^2).

$$\rho = (R * A)/l \qquad \textbf{(3.2)}$$

Where ρ is Resistivity of ceramic

A – Area of cross-section of disc

l - Length of ceramic disc

The significance of the electrical resistivity-temperature measurements in PTCR sensors is, through the application of the non-linear jump in the resistivity near the Curie temperature, where the PTCR sensor materials are utilized to fabricate devices for current limiting or current over load protection [73] and also in various applications as mentioned in chapter 1.

3.6 Impedance Spectroscopic Measurements

The Impedance is the over all complex resistance of a capacitor with input voltage. Impedance spectroscopy is an electrical characterization technique used to determine the grain and grain boundary resistivity values with frequency. The impedance ($Z = Z' + i Z''$) vs. frequency measurements are made. The significance of impedance measurements includes measuring the potential barrier height and the concentration of the acceptor states at the grain boundaries. Chemisorbed oxygen ions are responsible for grain boundary acceptors states that create potential barriers and the PTCR effect.

Capacitance-Temperature, Impedance (Z) measurements with respect to frequencies were made in the range of 1Hz to 10MHz at room temperature using Agilent 4294A Precision Impedance Analyzer with a silicone oil bath and hot plate setup, temperature reading was monitored with K type thermocouple with (HP 34970A) Data Acquisition/Switch unit.

Chapter 4

Results and Discussion

4.1 Introduction

This Chapter discusses XRD, SEM, EDS analysis and the electrical properties of the materials. For the first batch of samples only XRD, SEM, and electrical properties were discussed, for the second batch EDS reports were also presented in addition to that of XRD, SEM and electrical properties of the materials. Two batches of ceramic sensors were produced at two different sintering temperatures 1100°C and 1350°C using calcination of mixed oxide method. The first batch of sensor with V-shaped NTCR-PTCR behavior with low sintering temperature and the second batch of sensor with PTCR behavior with higher sintering temperature were prepared respectively.

4.2 XRD patterns for Calcined Sensor

X-ray diffraction patterns for elemental analysis of the calcined ceramic sensor materials were carried out. XRD patterns were scanned in the 2-theta (2θ-degree) range of 20°-60° at room temperature. Both $BaTiO_3$ and La_2O_3 peaks were identified as primary and secondary peaks as shown in the figure 4.1. The tetragonal peak splitting [0 02], [2 0 0] for $BaTiO_3$ were also shown in the figure.4.2 for different concentration of La_2O_3 (x=0.0005, 0.0010 and 0.0030 mol %).

The starting mixtures of lanthanum doped $BaTiO_3$ showed the presence of peaks at 2θ = 22.14, 31.52, 38.92, 45.34, 50.98 and 56.30. This was attributed to $BaTiO_3$, whilst peaks at ~26.46°, 26.74°,44.62°, 46.08°etc were attributed to La_2O_3. From the powder X-ray diffraction results it is observed that as the donor concentration of the L_2O_3 increased, there is an increase in the lanthanum peaks near tetragonal splitting. Lattice parameter (a, c) values along with tetragonal distortion (c/a) values are shown in the table 4.1 for different concentration of lanthanum doped $BaTiO_3$ PTCR sensors. The cell parameters from JCPDS files for $BaTiO_3$ are listed as a= 3.9940 A°, c= 4.0380 A°. A little bit of variation is observed from the present values with that of standard JCPDS files. In general a solid solution series often (but not allways) shows a small variation lattice parameters with composition [154]. For the present composition, the same values of lattice parameters (a,c) and also same values of tetragonal distortion (c/a ~ 1.0732) are obseved. This is expected due to unreacted part of lanthanum near tegragonal splitting. The over all XRD pattens indicate that the decreasing lanthanum peaks and evolution of $BaTiO_3$ peaks attributed to incorporation of lanthanum into the $BaTiO_3$.

Table 4.1. XRD data for Calcined La_2O_3 doped $BaTiO_3$ at 1100°C/5Hours

Compound	**a (A^0)**	**c (A^0)**	**c/a (Tetragonal Distortion)**
$Ba_{0.9995}La_{0.0005}TiO_3$	3.99682	4.02896	1.0732
$Ba_{0.999}La_{0.001}TiO_3$	3.99682	4.02896	1.0732
$Ba_{0.997}La_{0.003}TiO_3$	3.99682	4.02896	1.0732

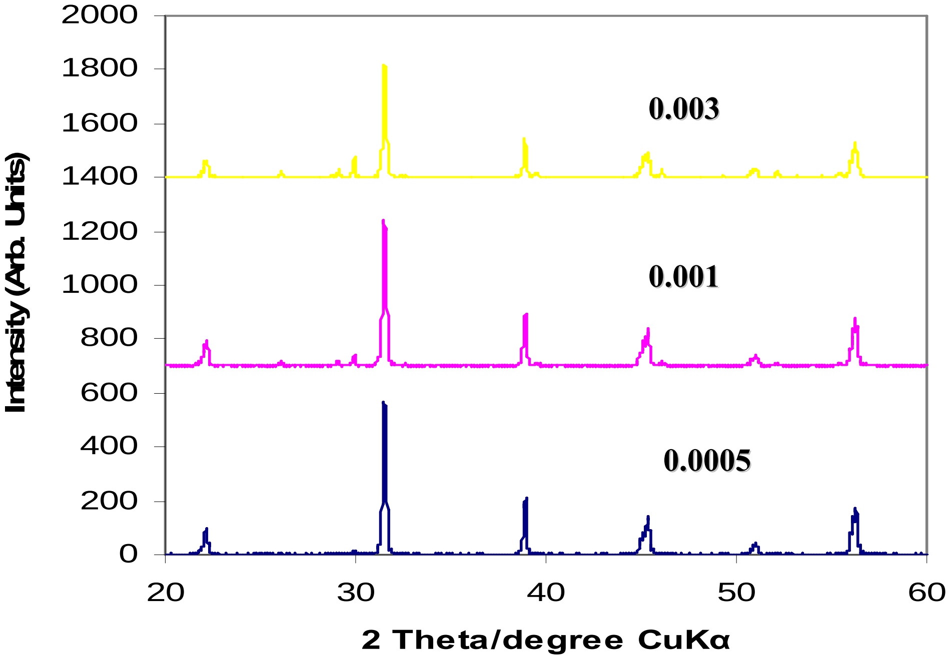


Figure 4.1. XRD patterns for calcined (a) 0.0005, (b) 0.001, (c) 0.003 mol% La_2O_3 doped $BaTiO_3$.

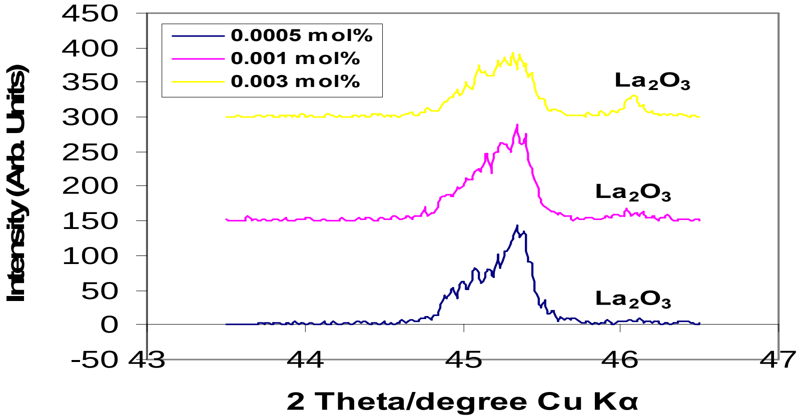


Figure 4.2. Tetragonal [2 0 0], [0 0 2] peaks for (a) 0.0005,(b) 0.001, (c) 0.003 mol% La_2O_3 doped $BaTiO_3$.

4.3 La_2O_3 doped $BaTiO_3$ with low sintering temperature

The resistance values for La_2O_3 doped $BaTiO_3$ pellets were measured using a 4 point probe technique. The resistivity values were calculated from the measured resistance and pellet dimensions. Typical Resistance-Temperature (ρ-T) curves for different concentrations of donor doped $BaTiO_3$ sintered at 1100°C with positive temperature coefficient of resistance are shown in fig.4.3. La doped barium titanate pellets made from ordinary solid state synthesis route, sintered at 1100°C showed V shaped NTCR-PTCR behavior. Electrical resistance behaviour of samples is divided into 2 regions, where in region I, temperatures ranging from 20°C to 100°C shown negative temperature coefficient of resistance (NTCR) effect with a mega-ohm resistance values and this region is called ferroelectric region. In region II with temperatures ranging from 100°C to 140°C materials shown an abnormal raise in electrical resistance values is observed and this region is called paraelectric region.

Almost all the samples showed a ferroelectric-paraelectric transition temperature approximately at 100°C (+/-) 5°C. As the lanthanum concentration increases the Tc value for BLT1-BLT3 concentrations are observed at the 100°C, with a slight increase in Tc for BLT4 and then for BTL5 Tc considerably decreased. This decrease in the transition temperature for the present La doped $BaTiO_3$ sintered at 1100°C, is expected due to lowering of sintering temperature and time, which is attributed to incomplete densification.

From previous research Samara *et al.* [155] reported that the linear decrease in Curie point is due to increase in hydrostatic pressure, and believed that impurities and domain orientation are also responsible for the change in Curie temperature. According to Jaffe *et al.* [142], the transition temperature generally called Curie temperature where the tetragonal-ferroelectric phase and the cubic paraelectric phase is dependent on the presence of impurities and stress levels for pure $BaTiO_3$. The ferroelectric phase transition temperature (Tc) in ferroelectric materials can be affected by many factors, such as modification of chemical composition, particle size, hydrostatic pressure, crystal imperfections and deviation from stoichiometry [139], where as a decrease in Tc of 40°-50°C in reduced $BaTiO_3$ was reported by Härdtl *et al.* [140].

The pellets displayed a room temperature resistance of 6 orders of magnitude with a negative coefficient of resistance effect. Only a very small change in resistive jump is observed in almost all the samples sintered at 1100°C, with a little abnormality in the BLT3 sample. Secondary thermal treatment of the samples at 400°C for 1 hour did not show any improvement in either in reducing the room temperature resistance or enhancement in resistivity values at the Curie temperature throughout the concentration range.

Low resistivity behavior at the room temperature is attributed to the ferroelectric domains oriented in such a way as to cancel the accumulated charge that is the electron trapping nature [3, 79, 141]. Even though all of the La_2O_3 doped $BaTiO_3$ compositions showed a little raise in resistance around the transition temperature. The high room temperature resistance keeps the jump small and these materials show V-shaped NTCR-PTCR multifunctional cryogenic sensor behaviour with a strong negative coefficient of resistance effect at room temperature [142]. For good PTCR thermistor it would be desirable to lower the room temperature resistivity while maintaining high grain boundary resistivity and PTCR jump [5]. From the present results it is revealed that high room temperature resistivity values with NTCR behavior are attributed, due to improper densification during sintering stage. The inhomogeneous distribution of donor dopant and doping was either partially successful or completely unsuccessful. Figure 4.4 show the SEM photographs for 3 different concentrations (BLT1, BLT2, BLT5). From the morphologies the average grain size of the samples decreases as the concentration of the donor dopant increases. No grain growth anomaly is observed at low sintering temperature. The average grain size of the BLT1, BLT2, and BLT5 micrographs calculated using line intercept method are around 0.5µm.

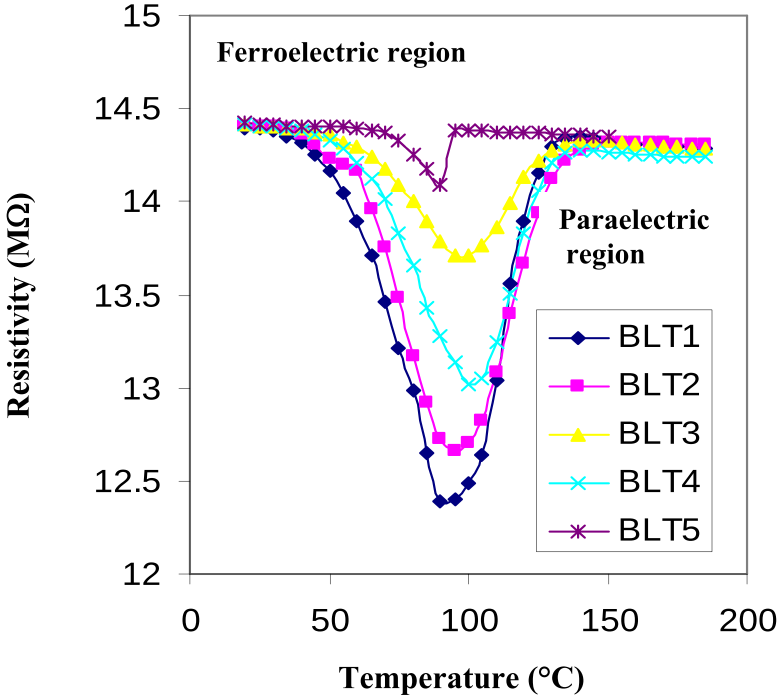


Figure 4.3. Electrical resistance vs. temperature behaviour of samples sintered at 1100°C.

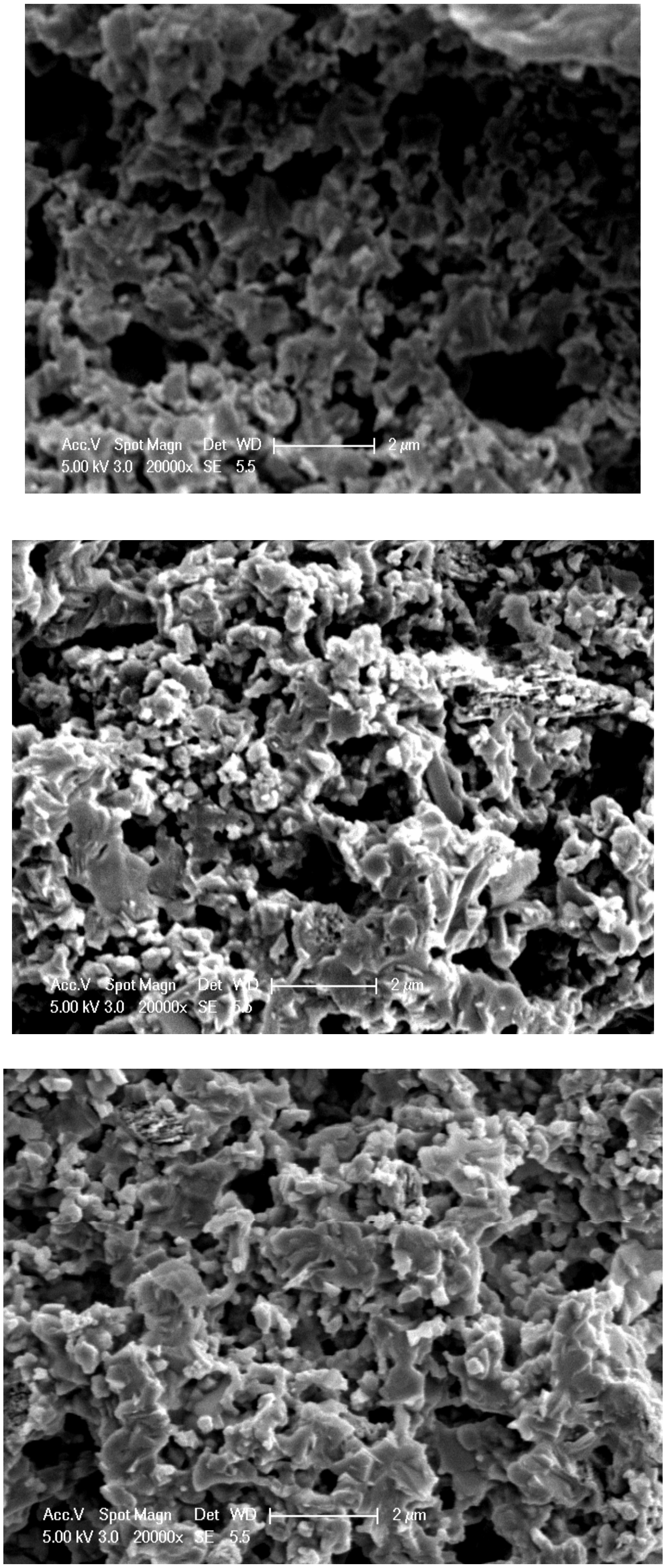


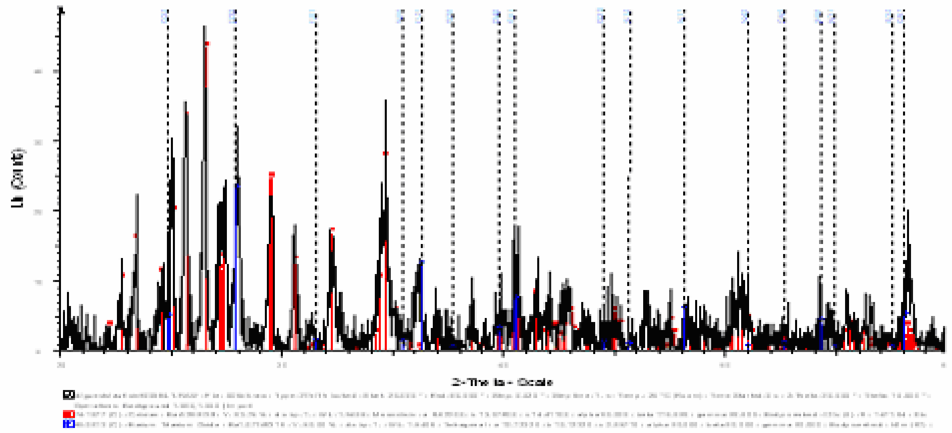
Figure 4.4. SEM photographs for BLT1, BLT2, and BLT5 samples sintered at 1100°C.

4.4 La_2O_3 doped $BaTiO_3$ sintered at 1350°C

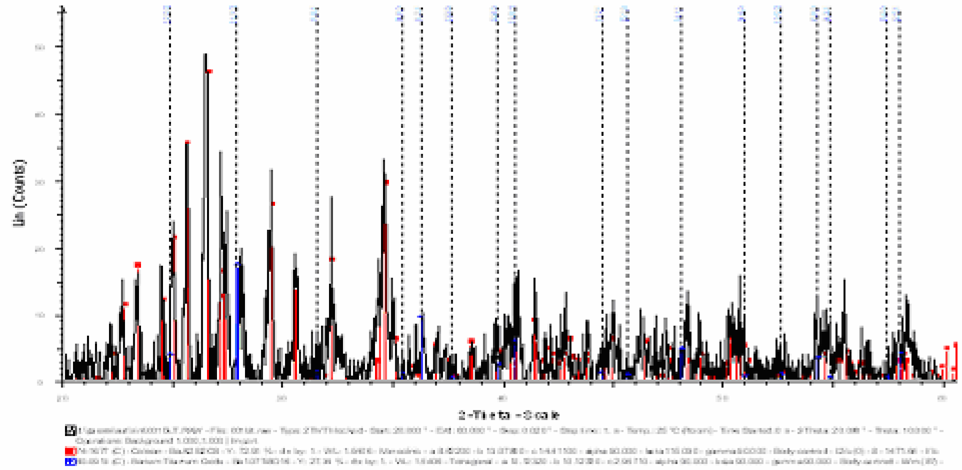
The effect of increase in donor, acceptor doping concentrations (x= 0.0005, 0.001, 0.003 mol% of La_2O_3 and 0.02, 0.04, 0.006 mol% of MnO_2) on insulating barium titanate with AST (Al_2O_3+SiO_2+TiO_2) as sintering aid was studied. Intimately milled raw materials were calcined at 1100°C for 5 hours as mentioned earlier. Calcined sensor material was again mixed with PTCR enhancer MnO_2 and also mixed with liquid phase sintering aid AST, and was milled for 24 hours with acetone medium and pellets were made with steel die. Different concentrations of La doped barium titanate were named as MBLT1, MBLT2, and MBLT3 which were sintered at 1350°C for 2 hours.

4.4.1 XRD Analysis

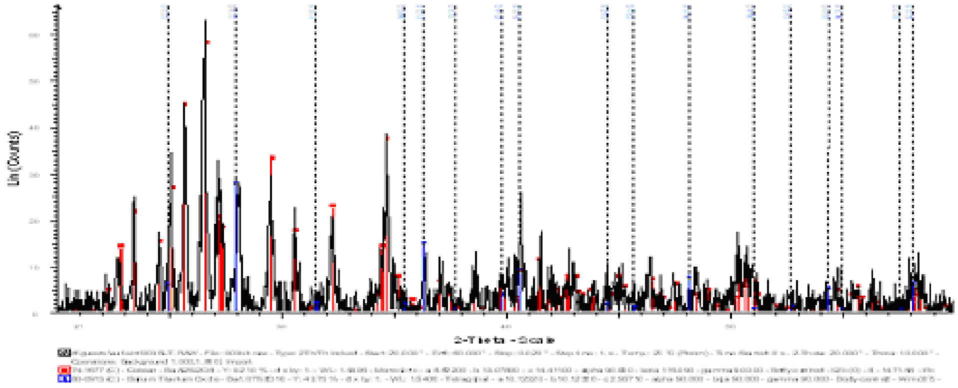
XRD patterns for Calcined sensor materials are shown in the figure 4.1. X-ray diffraction patterns for sintered samples were also obtained and were as shown in the figure4.5. Sintered Samples at 1350°C have shown two major phases, crystalline ceramic $BaTiO_3$ as a major primary phase and glassy Celsain ($BaAl_2Si_2O_8$) as minor secondary phase. Glassy secondary phase is expected due to liquid phase sintering aids and as well as excess reaction with the alumina-silicate crucible which is used in sintering process. Peaks with blue color are for $BaTiO_3$ and red color for glassy phased Celsain for MBLT1-MBLT3 were shown in figure 4.5, respectively.



(a) 0.0005 mol% lanthanum doped BaTiO3



(b) 0.001 mol% lanthanum doped BaTiO3



(c) 0.003 mol% lanthanum doped BaTiO3

Figure 4.5. XRD patterns for sintered (a) 0.0005, (b) 0.001, (c) 0.003 mol% La_2O_3 doped $BaTiO_3$ with AST as sintering aids.

4.4.2 Electrical Resistivity Behavior

The electrical resistivity-temperature behavior with the PTCR effect for La doped $BaTiO_3$ ceramic sensors is shown in Figure 4.6. This shows that higher dopant concentrations result in a sharp increase in resistivity. Also it is indicated that the Curie temperature T_c, for the sensor materials sintered at 1350°C shifts towards lower temperature values for all the 3 concentrations investigated in this work and it drastically dropped to 100 (+/-) 5 °C with that of the normal range of $BaTiO_3$ ~120°C. Further sensors at high sintering temperature have the same hydrostatic pressure effect on Curie temperature as discussed earlier section. This indicates an ionic compensation mechanism where charge imbalance is created when the replacement of Ba^{2+} by La^{3+} on the A -site is compensated by cation vacancies on the A- or B- site. The observed resistivity rise can also be attributed to surface oxidation of the grains during cooling of the La-doped $BaTiO_3$ ceramics after sintering at 1350°C in air, this results in oxygen non-stoichiometry [143].

Increasing resistivity jump with few orders of magnitude is also attributed to an increase in acceptor concentration of MnO_2 with that of sintering aids added for $x = ¾$ which is corresponding to molar ratio 4: 9: 3. According to Heywang's model [4,27], the double Schottky barrier inducing the PTCR effect is generated from grain boundary defects, which can trap electrons. There are two types of defects proposed; one is adsorbed oxygen and the other is Ba^{2+} vacancies.

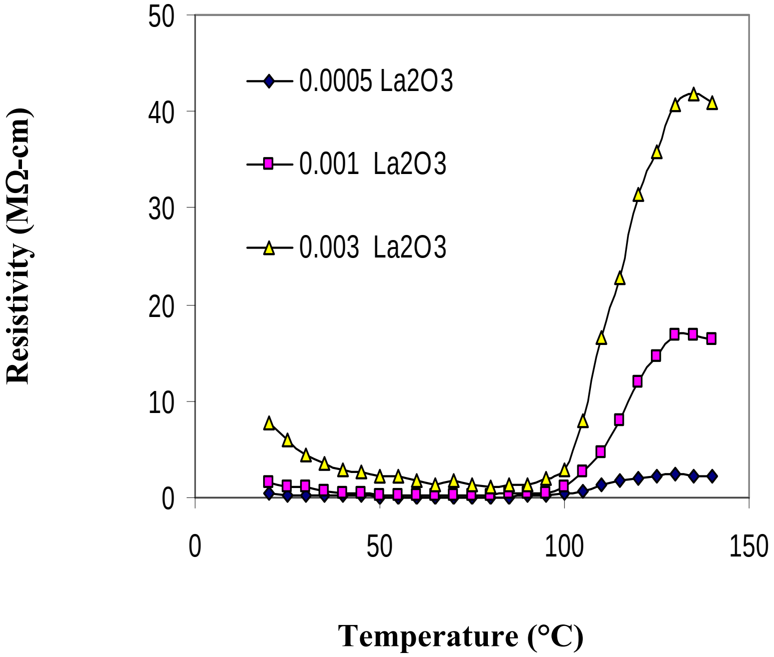


Figure.4.6. Electrical Resistivity as a function of temperature for the samples containing- MBLT1-0.0005, MBLT2- 0.001, MBLT3-0.003 mol% of La_2O_3 doped $BaTiO_3$.

Sintered pellets with dense crysatllograhpic structure were as shown in the SEM micrographs figure4.8, however the room temperature resistivity measurement revealed that doping was partially successful, due to the fact that the room temperature resistivity remained high. These results indicated that even at low donor dopant concentrations either substitution was partially sucessful or electronic compensation does not occur and charge imbalance is compensated by the creation of the A site vacancies. The defect that dominates the PTCR effect cannot be identified from the present result. A previous study [144], has indicated that a switch in the compensation mechanism from an electronic compensation at low dopant concentration to an ionic compensation causes an increase in room temperature resistivity at higher dopant concentrations. However, the reason for the switching in the compensation mechanism is still poorly understood and remains unexplainable.

4.4.3 Impedance and Dielectric Behavior

As previously stated in the earlier chapter an impedance spectroscopy is an electrical characterization technique used to explain the grain and grain boundary resistivities of ceramic sensor contributions to electrical resistivity. Numerous experimental results illustrate that semiconducting $BaTiO_3$ with PTCR behavior is a grain boundary resistive phenomena. Impedance-frequency measurements on the ceramic sensors are shown in figure 4.7. This figure shows that the Z'' data are dominated by the low frequency response and suggests that the doped-$BaTiO_3$ ceramics can be described by a high resistance, low capacitance parallel R-C element model. This figure also resembles the Debye like peaks at low frequency region as presented else where in literature [56]. In general the impedance is an overall complex resistance and at low frequencies the real part of the impedance is dependent on both the grains and their grain boundary resistivity. As the frequency increases the real part of the impedance decreases, which is due to the insufficient time for electrons to completely jump over the potential barrier. Sensor with high La-dopant concentration show considerably higher impedance which is due to the presence of the high resistive grain boundaries. Semi conducting $BaTiO_3$ PTCR effect is dependent on the sensors dielectric constant or permittivity (k') as a function of temperature. The height of potential barrier is inversely proportional to the dielectric constant of the sensor material. The thickness and diameter of the sensor materials were measured before electroding inorder to calculate the dielectric constant of the material.

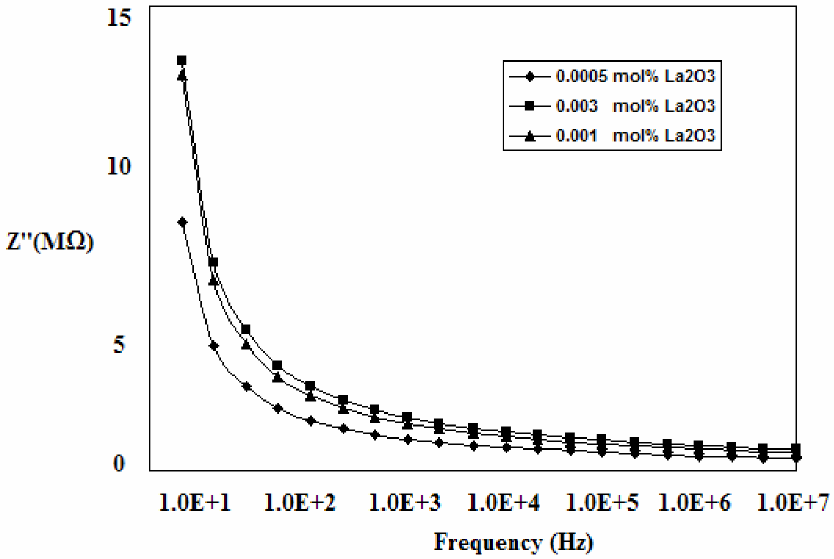


Figure.4.7. Bode plot for Z'' vs. Frequency at room temperature for sintered at 1350°C

The sintered pellets were electrode with silver epoxy paste and the pellet was fired at 200°C for 4 hours. For capacitance measurement pellets were place in a silicone oil bath setup. The dielectric constant as a function of temperature for different donor concetrations of lanthanum was obtined for smaples MBLT1-MBLT3 and was obtained at fixed frequency that is at 1 KHz and whose results were shown in figure 4.8. From this figure it is indicated that the higher values of dielectric constants were observed for intial concentrations of donor dopants. As the concentration of the latter reaches maximum 0.003 mol% in the present case, the dielectric response is drastically decreased. In general ceramic materials that with dielectric constant (ε_r<= 30), electrical resistivity (ρ) >= 10^{12} (Ω-cm), dissipation factor (tanδ) <= 0.001, dielectric strength (DS) >= 5.0 kV/mm and dielectric loss factor (ε''_r) <= 0.003 at 25°C are usually classified as good insulators.

Ceramic materials such as ferroelectrics, ferrites and sensor types such as PTCR, varistors, and ceramic thermistors which exhibit nonlinear response to changes in applied field or temperature, and for which insulating characteristics, though important, are often of secondary consideration [156].

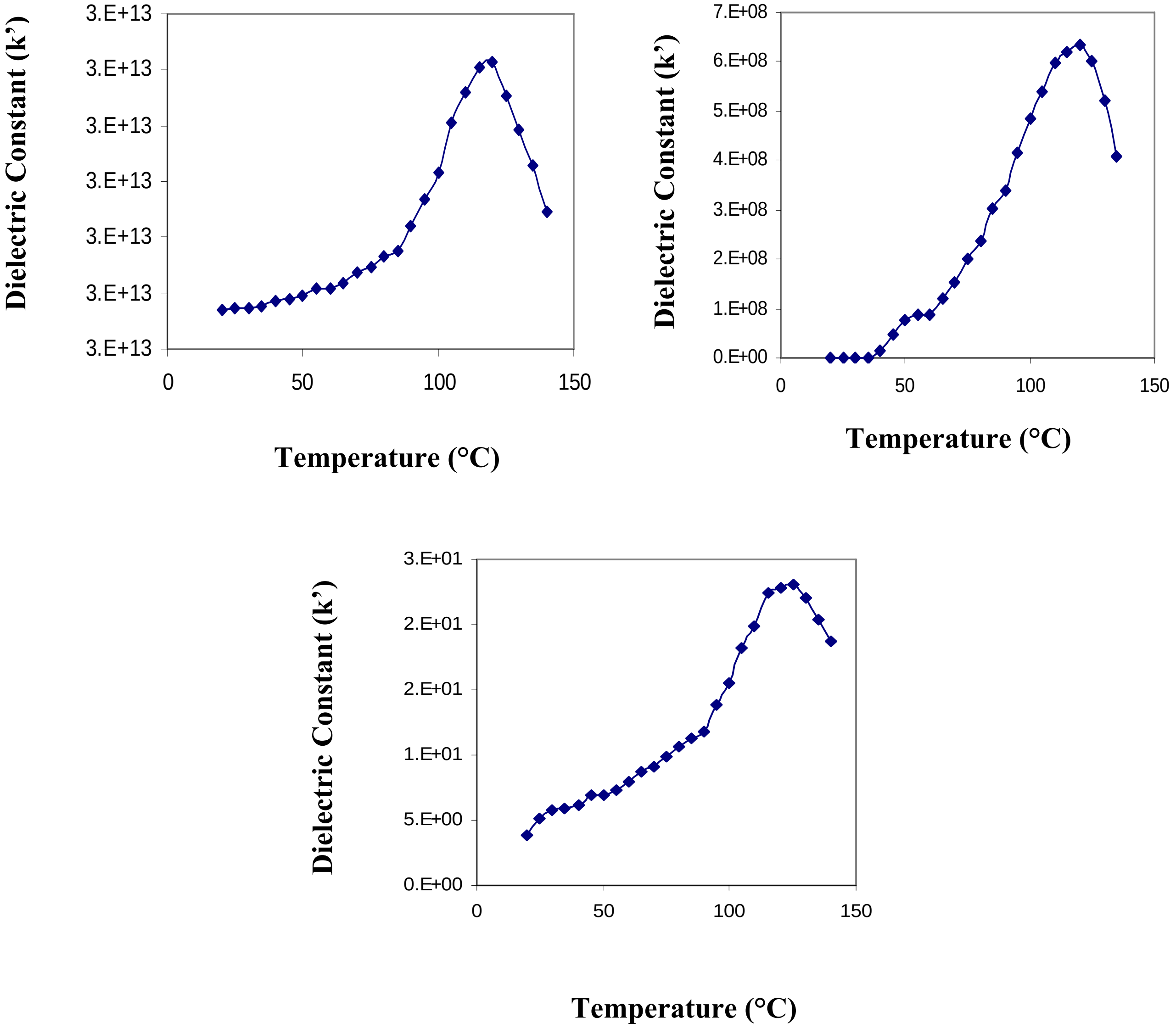


Figure 4.8. Dielectric constant-temperature curves for a) MBLT1-0.0005, b) MBLT2- 0.001, c) MBLT3-0.003 mol% of La_2O_3 doped $BaTiO_3$.

4.4.4 SEM characterization

Philips XL30S Field Emission Gun was used to obtain SEM photographs at a voltage of 5.0 kV with spot size 3, and for different magnifications. SEM micrographs of the fractured lanthanum doped $BaTiO_3$ surfaces for MBLT1, MBLT2, and MBLT3 with 20000 magnifications are shown in the figure 4.9. The average grain size of the MBLT1, MBLT2, MBLT3 micrographs calculated using line intercept method are around 5-10μm. It can be seen that the grains are not uniform in size and that the size increased with glassy ceramic flakes by forming matrix grains for some grains. It is also observed that all the concentrations of the material contain pores, with increasing porosity from MBLT1 to MBLT3. These porous samples with abnormal grain are identified with grain size 2μm on scale bar. Unexpected pores in the morphologies of SEM photographs are due to grinding effects.

From the literature, it has been observed that the porous n-$BaTiO_3$ can be prepared by incorporating organic polymers like Poly-vinyl-alcohol (PVA), Poly-vinyl-butyral (PVB), Poly-ethylene-glycol (PEG). This can be done by incorporation of graphites, borides, carbides or silicides to barium titanate [145,146]. Also thermal decomposition of barium titanyl oxalate ($BaTiO\ (C_2O_4)_2\ H_2O$) [147, 148] and partially oxidized Ti powders to $BaTiO_3$ have been reported to exhibit high PTCR effect [8]. Adsorption of oxygen at grain boundaries to form surface acceptor states is due to the presence of pores in porous ceramics than ordinary dense ceramics [153].

Elemental analysis was done by EDS analysis for fractured surfaces are shown in figure 4.10. In this figure La, Si, Al, Mn with Ba is identified.

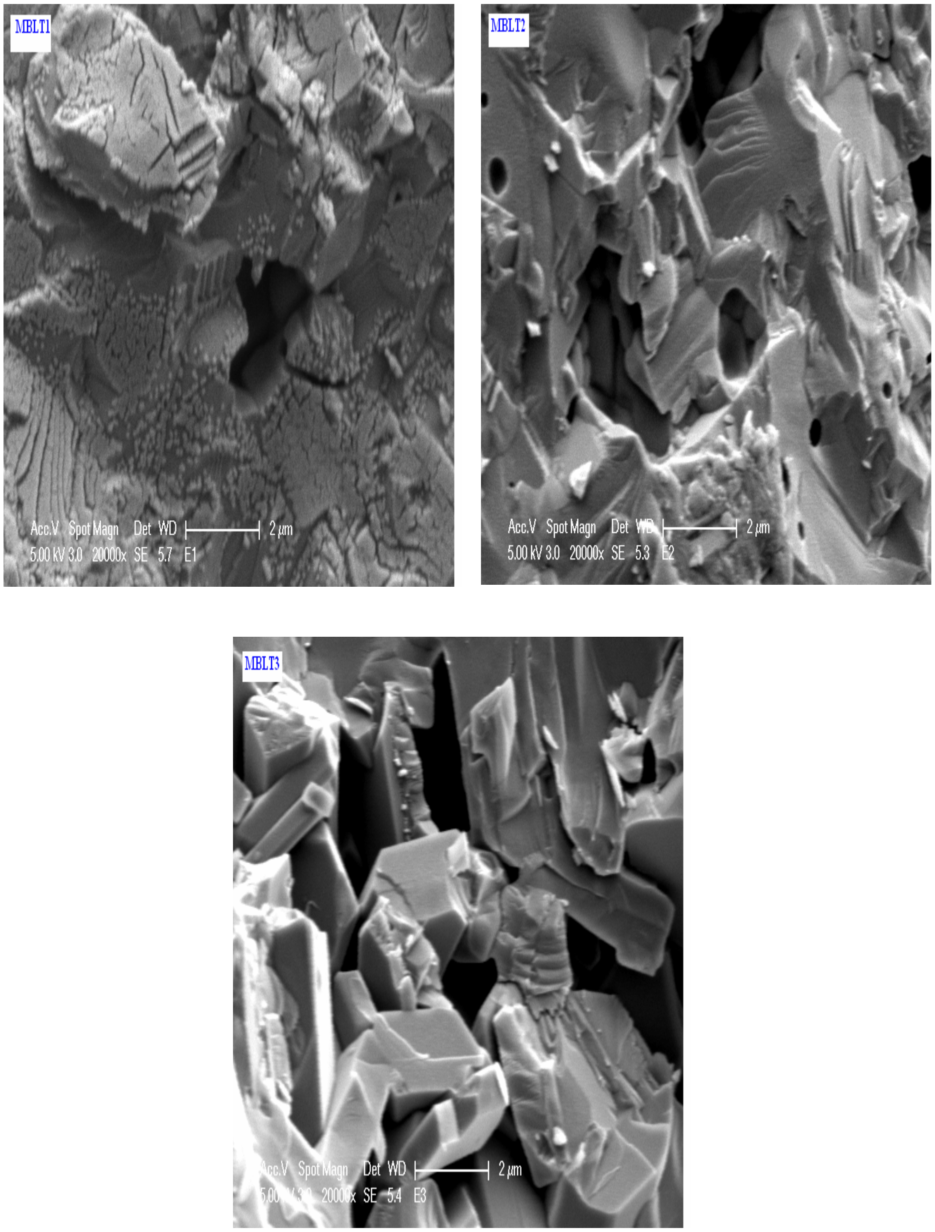


Figure 4.9. SEM photographs for La-doped $BaTiO_3$ ceramic surfaces showing their micro structural changes for MBLT1-MBLT3 sintered at 1350°C, Scale bars are 2.0μm for all the three concentrations.

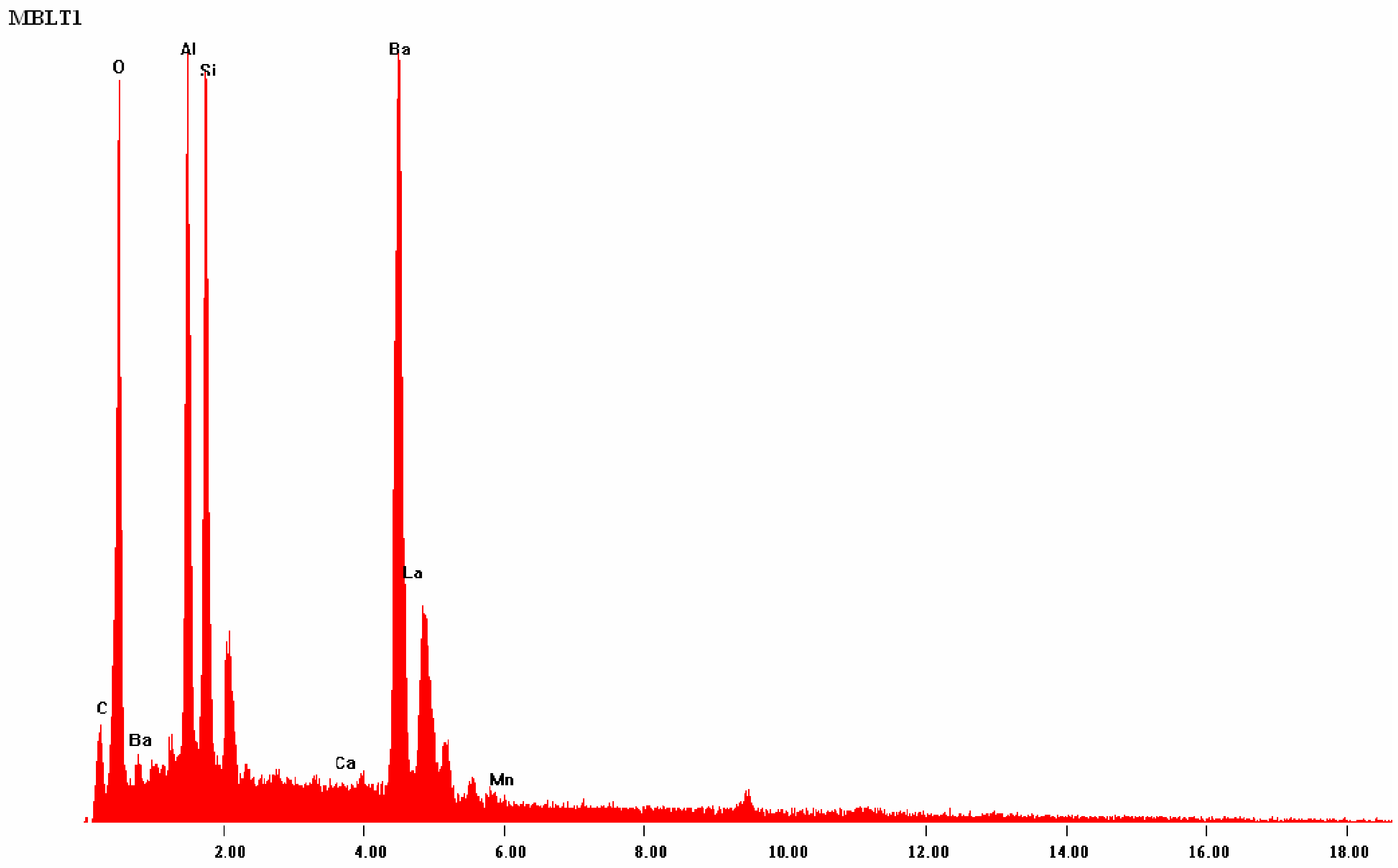


Figure 4.10 (a) : EDS peaks for La-doped BaTiO3 ceramic for MBLT1

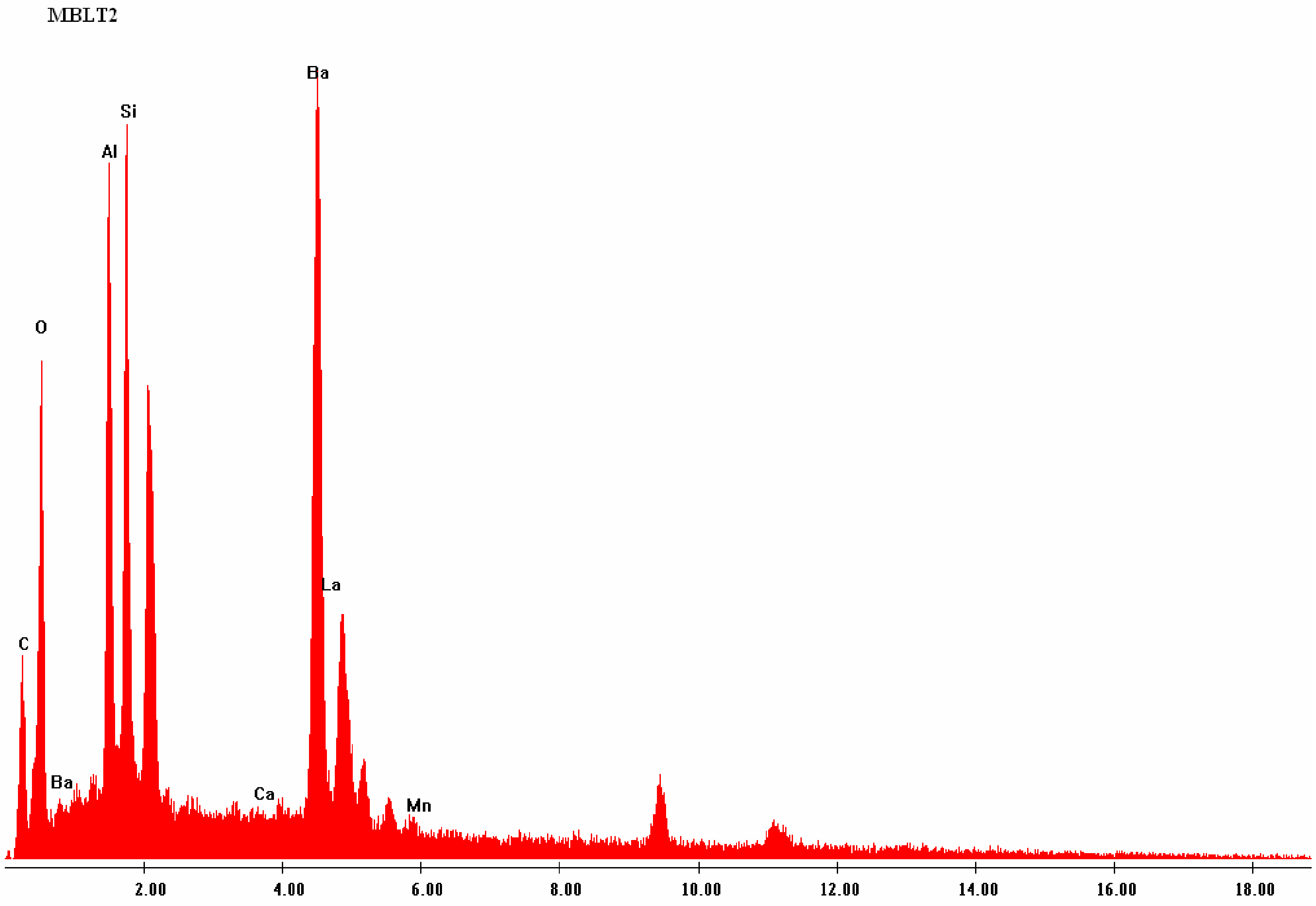


Figure 4.10 (b) : EDS peaks for La-doped BaTiO3 ceramic for MBLT2

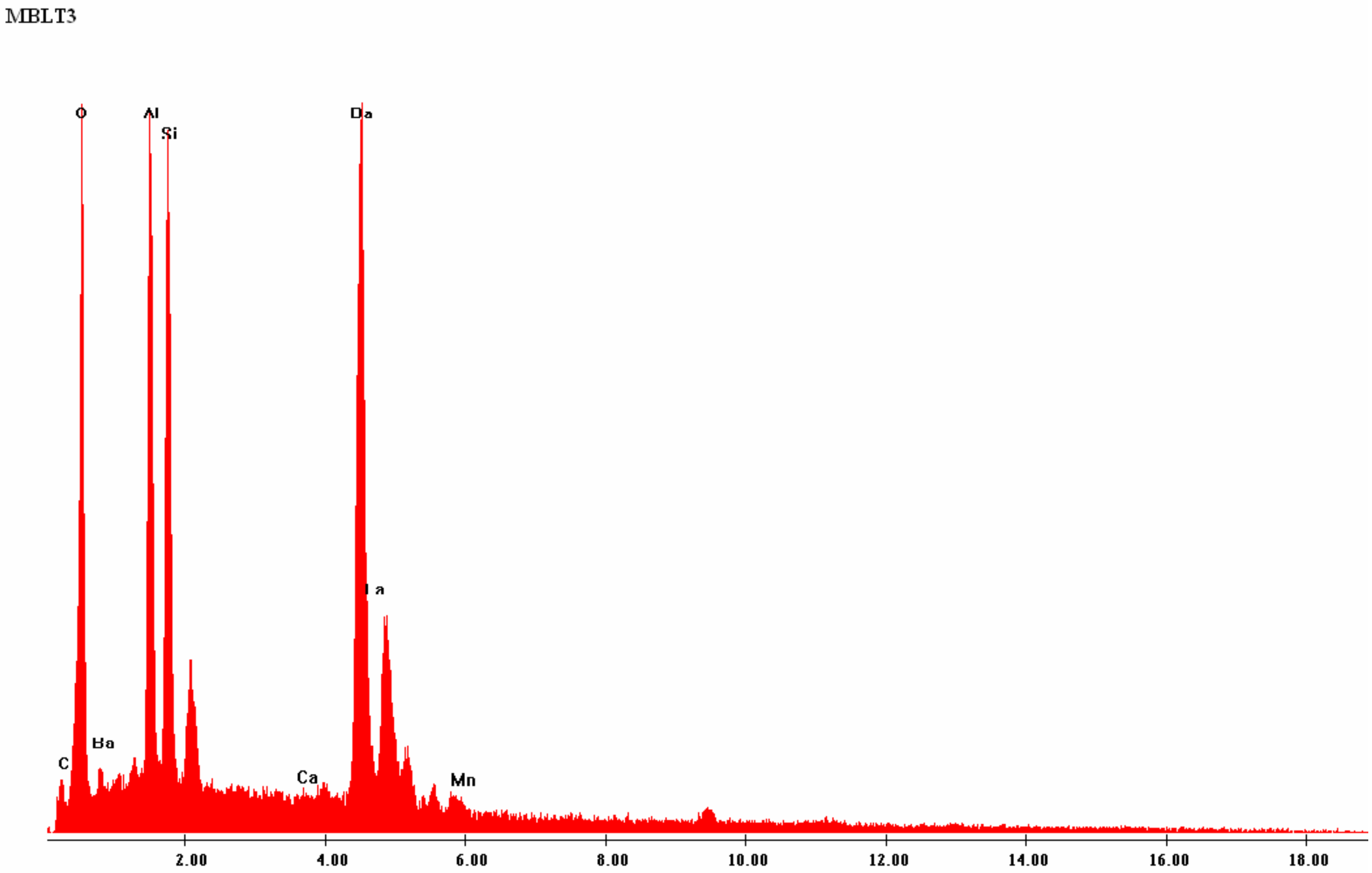


Figure 4.10 (c) : EDS peaks for La-doped BaTiO3 ceramic for MBLT3

Chapter 5

Conclusion and Recommendations

5. 1 Conclusion

This thesis investigated the possible candidate for PTCR sensor materials. From the primary investigation and material analysis it is identified:

1. $BaTiO_3$ doped with La_2O_3 and sintered at 1100°C show V shaped NTCR-PTCR behavior.
2. For the first batch of sensor materials, the resistivity results indicate a relatively high room temperature resistivity which increased with increasing concentration of lanthanum.
3. Higher resistivity values at room temperature are expected due to the unreacted part of lanthanum donor dopant.
4. The size of the PTCR jump is relatively small.
5. First batch of samples with V-Shaped NTCR-PTCR behavior are attributed to multifunctional cryogenic sensor applications.

For present investigations the small size of the PTCR jump and the high room temperature resistivity values leaves the area of improvement for lanthanum doped $BaTiO_3$ ceramics with low sintering temperature.

For the second batch of sensor materials:

1. $BaTiO_3$ doped with La_2O_3, with liquid phase sintering aids sintered at 1350°C show PTCR behavior.
2. Higher resistivity values at room temperature are expecting due to unreacted part of lanthanum donor dopant.
3. From XRD values, lanthanum peaks near tetragonal peak splitting are also due to un-reacted part of donor dopant.
4. Enhancement in the PTCR effect and reduction in Curie temperature values with increasing donor concentration are due to increasing acceptor concentration (MnO_2) and also with liquid phase sintering aids.
5. The abnormal grain growth is especially due to the addition of sintering aids SiO_2 and TiO_2.

The compensation mechanism which causes these effects when donor dopant and acceptor co-dopants are added is still unclear and should be further studied. Understanding this mechanism gives a possibility of improving physical behavior and will open up new applications for PTCR ceramic sensors. Through understanding of Impedance Spectroscopy for electrical properties at different temperatures and frequencies is needed.

As mentioned earlier, low room temperature resisivity values are necessary for PTCR materials at all sintering temperatures for all possible commercial applications. At present due to high room temperature resistivity values of lanthanum doped $BaTiO_3$ with higher and lower sintering temperatures, we were in find of new fabrication mechanism and processing conditions. Due high resistivity values at room temperature for present research we have not much concentrated in obtaining the electrical properties and specially Impedance mmeasurements for present thesis. Such type of NTCR effect with high electrical resistivity values at room temperature is a dangerous sign for PTCR materials. Our future aim is to reduce the room temperature resistivity values by lowering the sintering temperature.

5.2 Recommendations

The ultimate goal of the present project is to reduce the sintering temperature of PTCR ceramic sensors by reducing room temperature resistivity values considerably to lowest orders (~ 10^1-10^2Ω-cm) of magnitude at low sintering temperature. Obtaining PTCR behaviour in feeroeletric materials is a diffucult process. Especially due to compositional variations with impurity concentrations, sintering temperature differences, aging, which ultimately leading to microstural changes in the entire material with changes in electrical properties.

The following are few recommendations for future research:

(1) Comprehensive and thorough understanding of literature is needed.

(2) Impurity concentrations and processing conditions play a major role in PTCR sensor manufacturing, so 100% purity of the material is needed for PTCR sensor fabrication.

(3) At most care is need in taking minute particles of donor dopants for achiving semi conducting behavior, otherwise excess amount of donor will be the make the sensor again an insulator.

(4) Need to avoid unexpected contaminations from milling media, such as type of balls used in milling and jar that is used for milling.

(5) Thorough understanding of different sintering mechanism is another important issue for PTCR snesor fabrication and also need to re-consider the sintering processes used in sensor prepartion.

Future work could be in the area of reducing sintering temperature by lowering the room temperature resisitvity with higher orders of mangituede resistivity raise and also reduing sintering time. A novel method of sintering called microwave sintering is useful, promising and superior process as far as in reducing the sintering time, and less power consumption with good sintering characteristics in terms of densification, porosity etc.

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