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The Fabrication of Porous Barium Titanate Ceramics via Pore-Forming Agents (PFAs) for Thermistor and Sensor Applications

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1. Introduction

The perovskite family includes many titanates used in various electroceramic applications, for example, electronic, electro-optical, and electromechanical applications of ceramics. Barium titanate, perovskite structure, is a common ferroelectric material with a high dielectric constant, widely utilized to manufacture electronic components such as multilayer capacitors (MLCs), PTC thermistors, piezoelectric transducers, and a variety of electro-optic devices (Wang, 2002).

For positive temperature coefficient of resistance (PTCR) and humidity/gas sensing applications of BaTiO₃, a porous microstructure is required. When oxygen is adsorbed on the grain boundaries, PTCR effect is enhanced. Thus a porous structure is needed for PTCR properties. Besides, porous ceramics can also be used for humidity/gas sensing. The water vapour is adsorbed on pores improving the electrical conductivity of the surface.

A number of routes are employed in order to fabricate porous ceramics for PTCR and/or humidity/gas sensors. Low pressure forming can be used for the production of BaTiO₃ ceramics. Forming can be done by uniaxial pressing since hot pressing or hot isostatic pressing can eliminate pores. Also several other pressureless forming techniques can be used to make porous bodies. Another method for fabricating porous ceramics is using pore forming agents (PFAs) prior to sintering. PFAs form porosity through the ceramic body by different mechanisms. Different porosifiers that can be used for the production of barium titanate ceramics are starch based, carbon based, metallic or polymeric porosifiers. In the following paragraphs, crystal structure of, donor doping of and the electrical properties of barium titanate is described. Also the concept of porosity is briefly mentioned. Porous ceramics production, pore formers in general and pore formers in BaTiO₃ is also explained. Finally PTCR and humidity/gas sensing properties of BaTiO₃ is described in detail.

2. Perovskites and barium titanate (BaTiO₃)

ABO₃ oxides which adopt the perovskite structure form an important group of compounds possessing many useful and interesting physical properties. The idealized structure is cubic,

point group $m\bar{3}m$. The structure can be thought of in two ways. First, it can be viewed as being constructed from corner-sharing octahedral of oxygen ions, with the small B cations occupying the octahedral site and the much larger A cations occupying the interstices between the stacked octahedra. Alternatively, the structure can be thought of as close-packed ordered layers of oxygen and the larger A cations (AO_3), with the B cations occupying the octahedral interstices between the layers (Brook, 1991). The perovskite lattice of barium titanate is shown in Fig.2.1.

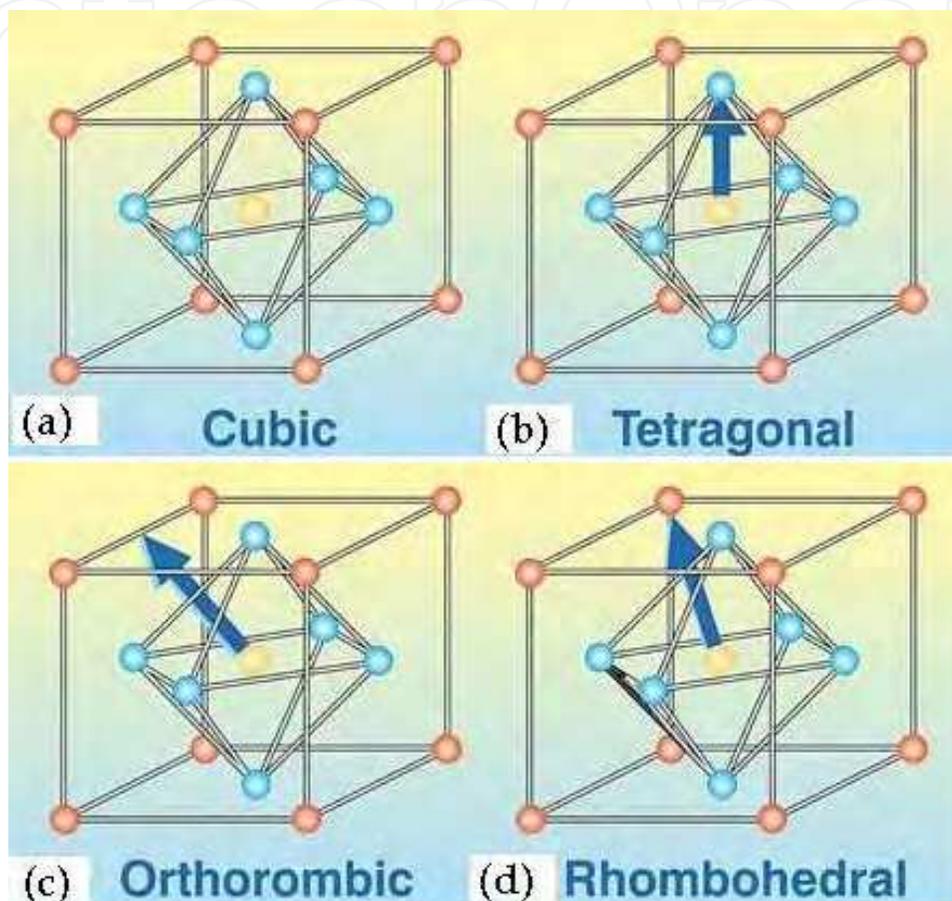


Fig. 2.1 The crystal structures of barium titanate ($BaTiO_3$). (b) [001], (c) [110], and (d) [111] directions (Hutagalung, 2011).

$BaTiO_3$ exhibits two basic structures, one being a ferroelectric, tetragonal, perovskite structure within temperature range 5-125°C. Above 125°C, the $BaTiO_3$ has the cubic perovskite, paraelectric phase ($a=4.009\text{\AA}$, $c/a=1$). $BaTiO_3$ exhibits a first-order displacive phase transition at 125°C from cubic ($m\bar{3}m$) to tetragonal ($4mm$) on cooling. This change is accompanied by an elongation in the [001] direction and a contraction along the a-axes. Below 5°C, $BaTiO_3$ has another displacive phase transition resulting in an orthorhombic ($mm2$) structure ($a=5.667\text{\AA}$, $b=5.681\text{\AA}$, $c=3.989\text{\AA}$). Associated with the phase change, there is a continuous change in the polarization direction, from parallel to the $\langle 100 \rangle$ direction of the unit cell, towards the $\langle 110 \rangle$ direction. At -90°C, $BaTiO_3$ is transformed into the rhombohedral crystal structure and the polarization direction becomes parallel to the $\langle 111 \rangle$ direction (Zhou, 2000). The change of the crystal lattice dimensions with temperature in $BaTiO_3$ is shown in Fig.2.2.

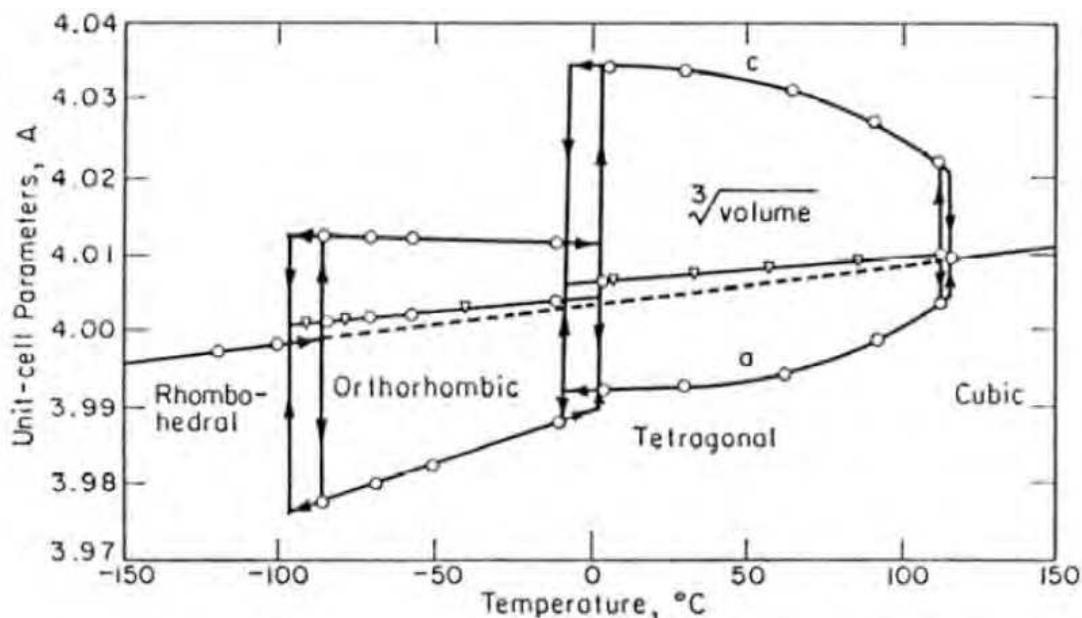


Fig. 2.2 Lattice constants of BaTiO₃ as function of temperature (Wang, 2002).

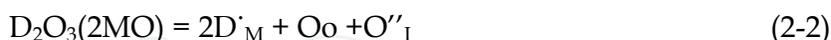
In an ideal cubic perovskite, the ionic radii, r_i ($i=A, B, O$), satisfy the relation $r_A + r_O = \sqrt{2} (r_B + r_O)$. The Goldschmidt tolerance factor for perovskites is, hence defined by

$$t = \{r_A + r_O\} / \{\sqrt{2} (r_B + r_O)\} \tag{2-1}$$

For pure barium titanate $t \sim 1.06$. t is greater than 1 due to the fact that the Ti^{4+} ion is smaller than its cavity (BaZrO₃ has $t \sim 1$) and/or that the Ba^{2+} is larger than its cavity (SrTiO₃ has $t \sim 1$) (Tsur et al., 2001).

2.1 Donor doping of BaTiO₃

In a stoichiometric solid solution the extra positive charge of a donor center can be compensated by a cation vacancy or an anion interstitial



Eq. (2-2) maintains a perfect cation sublattice, while the anion sublattice is perfect in Eq.(2-3). A shift from the stoichiometric solid solution with its compensation by a lattice defect, to a non-stoichiometric solid solution with compensation by an electronic defect, requires an interaction with the ambient atmosphere. The stoichiometric solution may gain or lose oxygen at oxygen activities greater than or less than, in equilibrium with the stoichiometric composition. In this way, The compensating lattice defect is eliminated and is replaced by electrons in the case of donor dopants (Smyth, 2000).

When La^{3+} replaces Ba^{2+} on the A-site (La is too large to replace Ti on the B-site), 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 follows





Ionic compensation ((2-4) and (2-5)) should have negligible effect on the room temperature conductivity due to the immobility of cation vacancies; La doped BaTiO₃ compensated in this way should, therefore, remain insulating. In contrast, electronic compensation (Eq. (2-6)) should cause a substantial increase in conductivity, in which the number of carriers equals the La concentration (Morrison et al., 2001).

Fig.2.3 indicates the effect of donor concentration (La³⁺) on the electrical conductivity and grain size of BaTiO₃. As the donor concentration increases initially the conductivity increases up to 0.15% of La³⁺ and then decreases up to 0.3% of La³⁺. The high conductivity region is where the electronic compensation dominates, after a critical donor concentration, cation vacancy compensation dominates and electrical conductivity decreases. Up to 0.3% of La³⁺, the grain size of BaTiO₃ is not affected by donor concentration being 25 μm, however, above 0.3% of La³⁺, grain size decreases to 5μm.

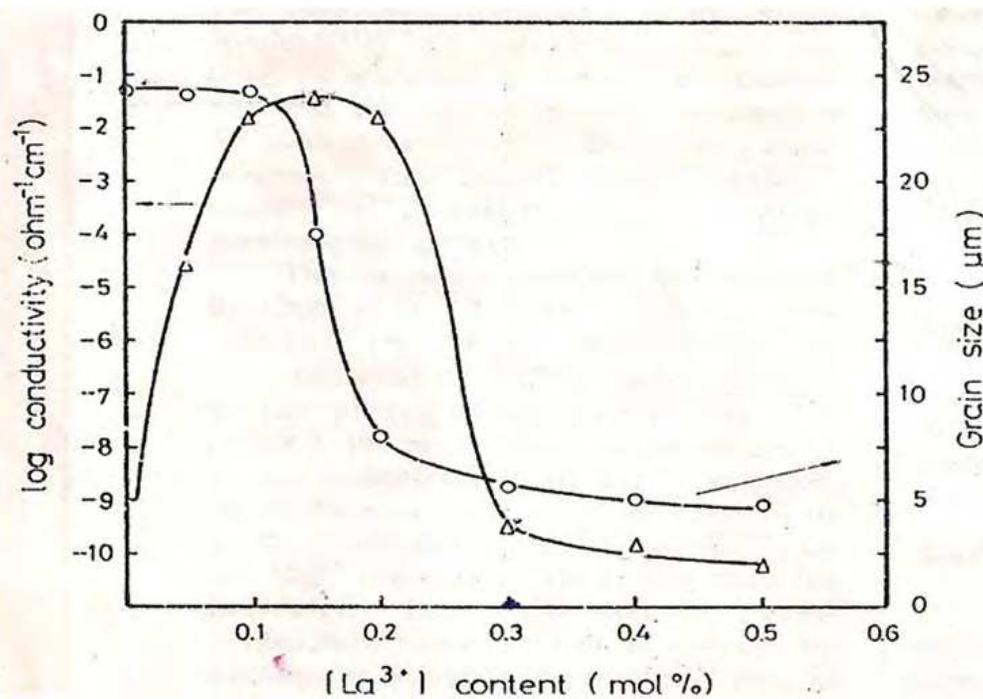


Fig. 2.3 Schematic of donor concentration influence on room temperature electrical conductivity and grain size.

Donor dopant incorporation is achieved by either electronic compensation at low concentrations or vacancy compensation at high concentrations. High concentrations of segregating donors at grain boundaries inhibits grain growth. At small concentrations, donor incorporation by electronic compensation explains the high conductivity. As the average dopant concentration increases, the local donor concentration at the grain boundary increases rapidly due to segregation. The donor incorporation at the grain boundary shifts from electronic to vacancy compensation, resulting in the formation of highly resistive layers and also, grain size decreases due to significant dopant drag on the boundary mobility (Desu, 1990).

3. Positive temperature coefficient of resistance (PTCR) property

Barium titanate is a very attractive material in the field of electroceramics and microelectronics due to its good characteristics. Its high dielectric constant and low loss characteristics make barium titanate an excellent choice for many applications, such as capacitors, multilayer capacitors (MLCs) and energy storage devices. Doped barium titanate has found wide application in semiconductors, positive temperature coefficient resistors, ultrasonic transducers, piezoelectric devices, and has become one of the most important ferroelectric ceramics (Vijatovic et al., 2008).

Barium titanate (BaTiO_3) is an insulator with a large energy gap of 3.05 eV at room temperature. It can be made n-type semiconducting by partially substituting Ba^{2+} by trivalent cations such as La^{3+} and Y^{3+} or Ti^{4+} by pentavalent cations such as Nb^{5+} and Sb^{5+} . The extra positive charge is compensated by free electrons. Doped BaTiO_3 which is sintered in air, exhibits a very high relative permittivity and a sharp increase in resistivity above Curie temperature, i.e. 120°C (called "positive temperature coefficient of resistance", or PTCR) when the structure changes from ferroelectric to paraelectric. Pure barium titanate is an insulator with no PTCR effect. A high PTCR effect can be achieved by the incorporation of transition metals such as Mn, V, Fe, Cu and Cr. This is because the transition metals substitute for Ti^{4+} as a lower valency state and act as acceptors (Kim, 2002; Kim et al., 2000; Park, 2004).

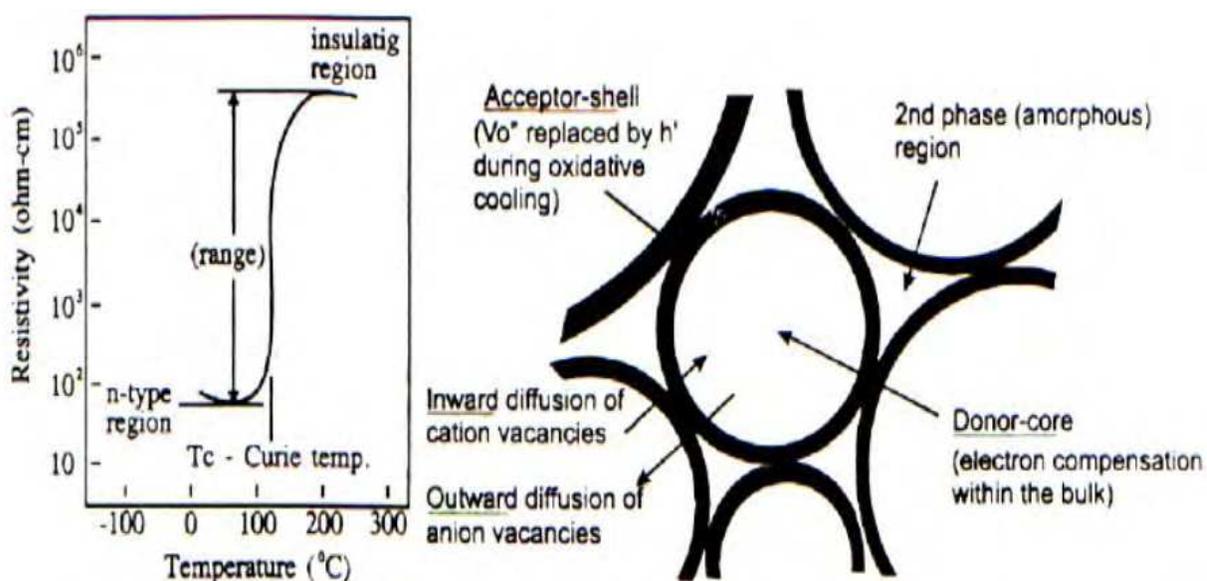


Fig. 3.1 Electrical resistivity for typical PTCR device and schematic presentation of defect chemistry responsible for PTCR effect (Vijatovic et al., 2008).

The grain-boundary model given by Heywang treats the grain boundary as a n-type Schottky barrier with deep acceptor states at grain boundaries (Vijatovic et al., 2008). The resistance anomaly behavior of doped BaTiO_3 is shown in Fig.3.1.

The double-Schottky energy barrier model proposed by Heywang is one of the most effective model which explains the mechanism of PTCR effect. According to this model, the double-Schottky type energy barrier is formed along the grain boundary and its barrier height determines the total conductivity. The electrical potential barrier results from

segregated acceptor ions or adsorbed oxygen at the grain boundaries. Sintering under vacuum or reducing gas atmosphere strongly reduces PTCR effect (Zhang, 2004).

Heywang explained PTCR effect in terms of potential barriers. The double Schottky barriers form at the grain boundaries. These barriers result from electron trapping by acceptor states at the interfaces. The acceptor states arise from segregated impurities at the grain boundaries or from adsorbed oxygen or from barium vacancies according to Heywang, Jonker and Daniels, respectively. Below Curie temperature in tetragonal BaTiO₃, barium vacancies are neutral but above Curie temperature vacancies trap electrons and become activated to singly ionised barium vacancies. Thus a negatively charged region forms at the grain boundary and a positively charged space region forms adjacent to the boundaries. A potential barrier is created between these two regions. Since trapped electrons are not available for conduction, the electrical resistivity increases around Curie temperature (Steele, 1991).

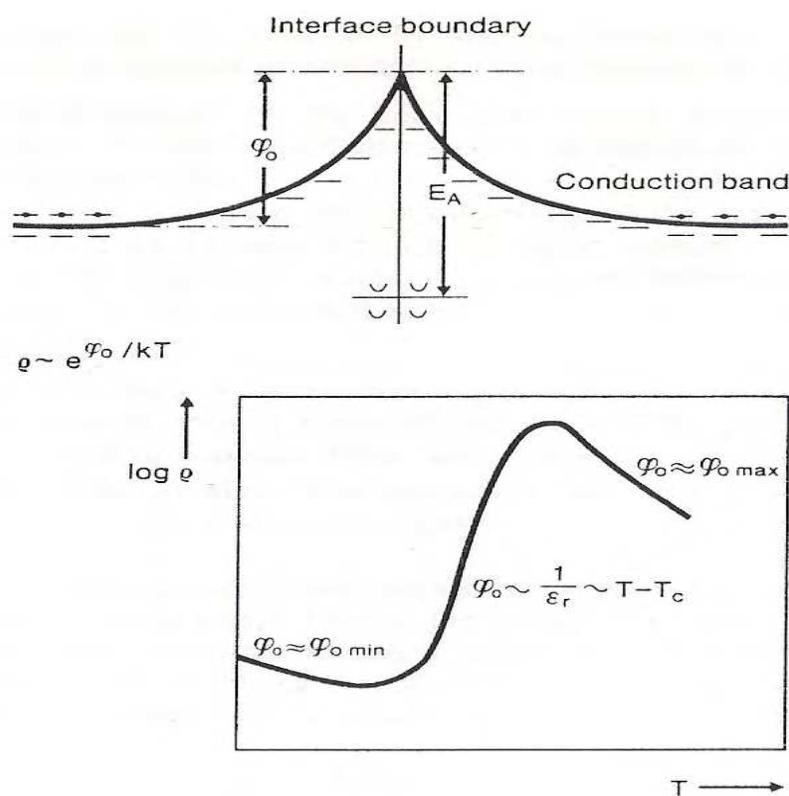


Fig. 3.2 The height of the potential barrier and the electrical resistivity-temperature curve (Steele, 1991).

The height of the potential barrier, φ_0 (shown in Fig.3.2) is given by

$$\varphi_0 = A / \varepsilon = A / C \cdot (T - T_c) \quad (3-1)$$

where A is a constant, ε is permittivity and T_c is the Curie temperature. Above T_c , the height of the potential barrier, φ_0 increases with decreasing ε (Steele, 1991). The electrical resistivity, ρ is directly proportional to the height of the potential barrier according to

$$\rho \sim \exp(\varphi_0 / k.T) \quad (3-2)$$

Thus the exponential increase of the electrical resistivity, ρ is

$$\rho \sim \exp A / C.k (1- T_c / T) \quad (3-3)$$

The barrier height of BaTiO₃ ceramics increases with increasing porosity. There is an exponential relationship between the resistance of PTCR ceramics and the barrier height. If the ferroelectric compensation of the ceramics at the room temperature is the same, the resistance of PTCR ceramics increases with increasing porosity. With the increase of porosity, the contact between individual grains looks more dispersed, which is helpful to diffusion of oxygen into the ceramic bulk and to oxidation of grain boundaries. A large PTCR jump is only possible for the samples sintered in an oxidizing atmosphere. The oxygen concentration at grain boundary is in direct proportion to PTCR effect of ceramics (Zhang, 2004).

Sintering under O₂ atmosphere affects not only barrier height but the resistance and capacitance of grain boundaries. The effect is due to variation of the adsorbed gases at the grain boundaries. The diffusion coefficient of oxygen at grain boundary is much higher than that in bulk, which implies that there is a gradient of adsorbed oxygen density in the surface of the grain. Sintering under O₂ atmosphere results in increasing number of oxygen acceptors at the grain boundary and increase in resistance. The barrier height also increases with sintering (Jiang, 2003).

3.1 Barium titanate as PTCR thermistor

Barium titanate, which has a perovskite structure, is a common ferroelectric material with a high dielectric constant, widely utilized to manufacture electronic components such as multilayer capacitors (MLCs), PTC thermistors, piezoelectric transducers, and a variety of electro-optic devices. Dielectrics and insulators can be defined as materials with high electrical resistivities. A good dielectric is, of course, necessarily a good insulator, but the converse is by no means true (Wang 2002). Barium titanate (BaTiO₃) is a ceramic material with a band gap of 3.05 eV at room temperature. Since the energy gap of barium titanate is large, it is an insulator when it is pure. It can be made *n*-type semiconductor when doped with donor dopants such as La³⁺ and Nb⁵⁺. Poly-crystalline *n*-type semiconducting barium titanate (BaTiO₃) exhibits a behaviour known as the positive temperature coefficient of resistivity (PTCR) effect. The electrical resistivity of *n*-type semiconducting barium titanate increases by several orders of magnitude near the ferroelectric Curie temperature (120 °C) (Kim 2000). At the Curie temperature, barium titanate undergoes ferroelectric to paraelectric transition (Kim 2004). This behaviour is indicated in Fig. 3.3 (Wang 2002). It has also been reported that single crystals of barium titanate exhibit negative temperature co-efficient of resistivity (NTCR) properties.

In fact, PTCR materials can be divided into four groups: polymer composites, ceramic composites, V₂O₃ compounds and BaTiO₃-based compounds (BaSrTiO₃, BaPbTiO₃...) (Wang 2002). Theoretical models of the PTCR effect have been proposed by both Heywang and Jonker. Both theories and experiments report that the effect is a grain-boundary related phenomenon (Park 2002). The grain boundaries of barium titanate show a large electrical resistance and PTCR results from the adsorbed oxygen at the grain boundaries. The porous ceramics exhibit large PTCR effect. According to Heywang, PTCR effect can be explained in

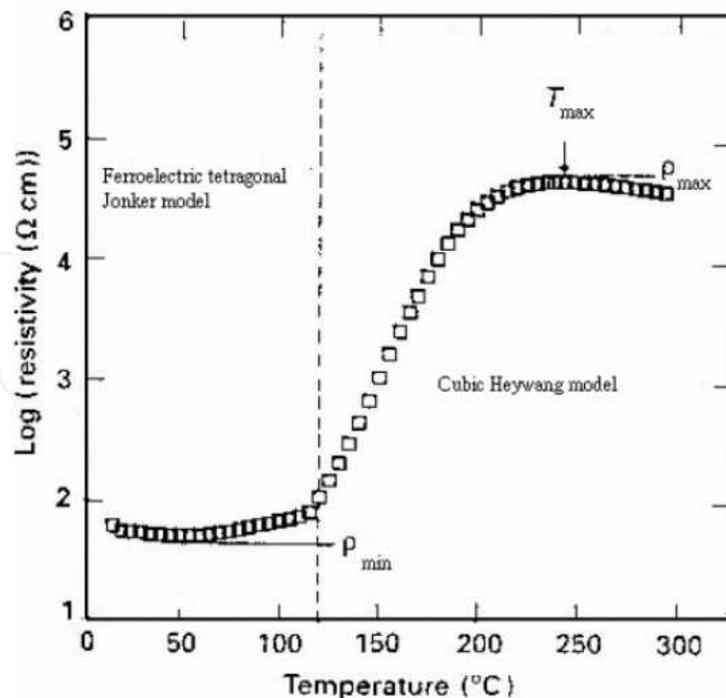


Fig. 3.3 Typical resistivity behavior of a BaTiO₃-type PTCR material (Wang 2002).

terms of temperature-dependent Schottky-type grain boundary potential barriers. These potential barriers result from charge accumulation due to grain boundary acceptor states such as segregated acceptor ions or adsorbed oxygen at the grain boundaries.

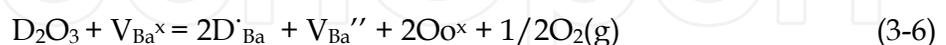
When the pure BaTiO₃ is sintered in air, the defect reaction is as follows:



Because of the high oxygen pressure at grain boundary when samples are sintered in air, this reaction prefers to happen at the grain boundary rather than in the grain lattice. The neutral barium vacancy may be ionized by the electron that was introduced by the donor dopant.



or



In pure donor doped BaTiO₃ ceramics (the microstructure is given in Fig. 3.4), the capturing of a free electron by neutral barium vacancy at the grain boundary during ferroelectric phase transition would respond for the PTCR effect (Qi, 2002).

PTCR effect can only be observed when barium titanate is sintered in air or oxidizing atmospheres. However, when it is sintered under vacuum or in reducing gas atmospheres, magnitude of the resistivity jump is reduced critically (Kim 2004). While the samples were annealed in reduced air (98% N₂ + 2% H₂), anion vacancies (oxygen vacancies) were generated and electron compensation would occur to maintain the electrical neutrality, increasing the conductivity of the ceramics. Heywang considered that no oxygen was

absorbed in the grain boundaries to form a depletion layer, and therefore that vacancy compensation (Ba compensation) was suppressed and the potential barrier was not built, the ceramic exhibited a poor PTCR effect. As the oxygen pressure increases, foreign ions are increasingly compensated by the oxidation process (formation of barium vacancies), and this Schottky barrier was formed between grains and grain boundaries to benefit the PTCR effect (Chen 2007). At low temperatures resistance is low since resistance is dominated by the grains. Above Curie temperature the resistivity of grain boundary increases PTC resistance. The disappearance of the domain structure above the tetragonal-cubic/ferroelectric-paraelectric transition temperature (T_c) results in the energy barrier being raised at all the grain boundaries (Wegmann 2007). Positive temperature coefficient (PTC) materials prepared from doped semiconducting barium titanate ceramics can be used in various kind of electronic circuitry as a switching device or as a constant temperature heater (Wang 2002).

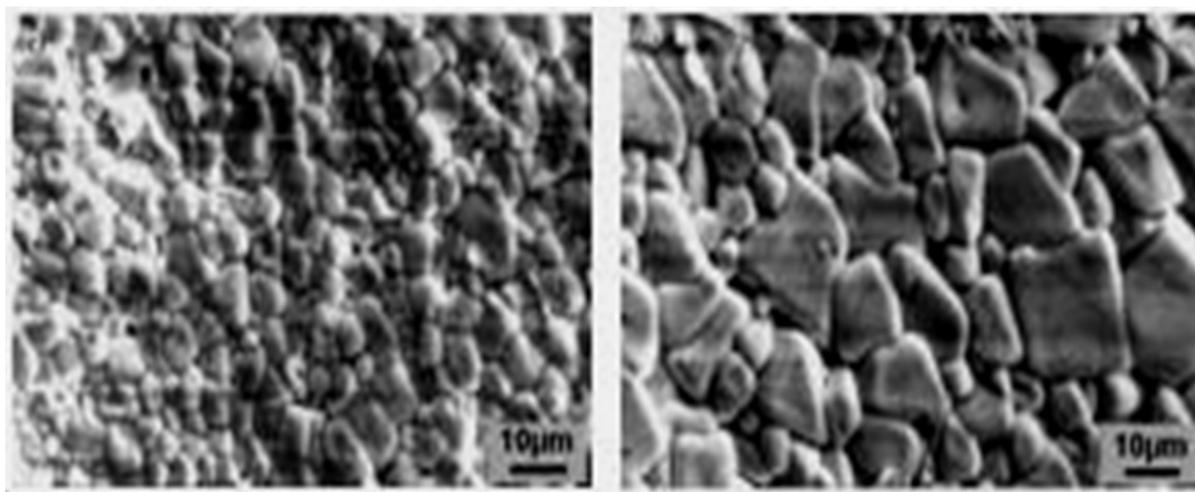


Fig. 3.4 The microstructure of BaTiO₃ based PTCR materials sintered at (a) 800C and (b) 1150C.

These PTC materials prepared from doped semiconducting BaTiO₃ ceramics can be used in various kinds of electronic circuitry as a switching device or as a constant temperature heater. Other important application of a PTC thermistor is the measurement/detection/control of temperature or parameters related to temperature. These PTC materials are known to have the highest temperature coefficient of resistance among all sensor materials available (Vijatovic et al., 2008).

4. Humidity/gas sensing

Even though the use of sensors is well established in process industries, agriculture, medicine, and many other areas, the development of new sensing materials with high sensing capabilities is proceeding at an unprecedented rate. Numerous materials have been utilized for humidity sensing, of which the metal oxides that are physically and chemically stable have been extensively investigated at both room and elevated temperatures. Sensors based on changes in resistance and capacitance, as shown in Fig.4.1, are preferred owing to their compact size, which could facilitate miniaturization required for electronic circuitry (Pokhrel et al., 2003).

These PTC materials are known to have a high temperature coefficient of resistance around Curie point and the ability of self-limiting, so they are as well come out to be a very useful device for sensor applications. The first semiconductor oxide gas sensors were reported by Seiyama et al. in 1962. Since then, there have been numerous studies concerning such oxide semiconductors as SnO_2 , ZnO_2 , In_2O_3 , TiO_2 , Fe_2O_3 , HfO_2 , and BaSnO_3 . They are nowadays widely used in the detection of gases. Semiconductor oxide gas sensors are extensively studied in order to improve their sensing characteristics, i.e., sensitivity, selectivity, stability, and response rate, to various kinds of gases and to meet the increasing needs of sensors in complicated systems and under strict conditions. A trial-and-error method is still mainly used in the development of new sensor materials to replace existing sensor materials (Park 2004). Metal-oxide-semiconductor (MOS) sensors operate on the basis of the modification of electrical conductivity of metal oxide layers, resulting from the interactions between O^{2-} , O^- and O^{2-} species and gas molecules to be detected (Kim 2005).

It has been known that absorption or desorption of a gas on the surface of a metal oxide changes the conductivity of the material. The sensitivity of a surface to a gas can be as low as parts per billion (ppb). It is highly desirable that metal oxide semiconductor sensors have a large surface area, so as to adsorb as much of the target analyte as possible on the surface, giving a stronger and more measurable response (especially at low concentrations).

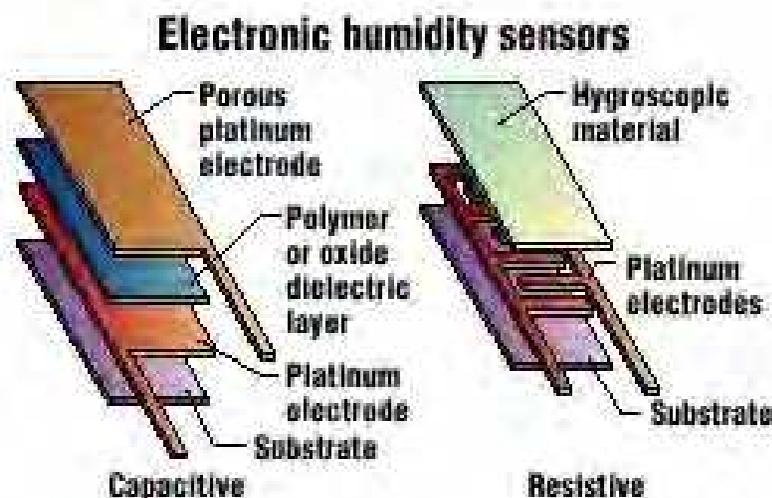


Fig. 4.1 Capacitive and resistive humidity sensors (Electronic Circuits and Projects Forum).

For n-type semiconductors, the majority charge carriers are electrons, and upon interaction with a reducing gas an increase in conductivity occurs. Conversely, an oxidising gas serves to deplete the sensing layer of charge carrying electrons, resulting in a decrease in conductivity (Fine 2010). Barium titanate is an n-type semiconductor which has humidity and gas (such as reducing gases) sensing properties (Park 2004, Wagiran 2005).

In recent years, solid state humidity sensors have been widely used for the measurement and control of humidity in an industrial or household environment. The relative humidity (RH), which is the ratio of actual vapour pressure of water to the saturated vapour pressure at a particular temperature, is commonly used to measure humidity. The sensor materials used are in general polymeric or ceramic. Ceramic humidity sensors are superior in performance to the polymeric type because of its stability towards a variety of chemical

species, wide range of operating temperatures and fast response to the changes of humidity. The principle of humidity sensing by ceramic sensors is changes of electrical conduction or capacitance due to water chemisorption and/or capillary conduction in the pores. The important ceramic materials used for humidity sensing are TiO_2 , $\text{Mg}_2\text{Al}_2\text{O}_4$, hematite, ZnC_2O_4 , perovskites. Perovskites such as (Ba, Sr) TiO_3 are protonic ionic conductors which have also been used for humidity sensing. In perovskite type oxides (ABO_3), the atoms on site A are susceptible to humidity (Agarwal and Sharma, 2002).

Perovskite oxides form a group of ceramics demonstrating a variety of interesting properties and promising applications. Some perovskite oxides, which are n-type semiconductors, such as doped SrTiO_3 ($\text{Sr}_x\text{La}_{1-x}\text{TiO}_3$), exhibit dependence of conductivity on humidity in the atmosphere they are exposed to. It has been proposed that H_2O molecules adsorb on the surface, and the adsorbed H_2O molecules can release electrons to the conduction band and consequently increase the electronic conductivity.

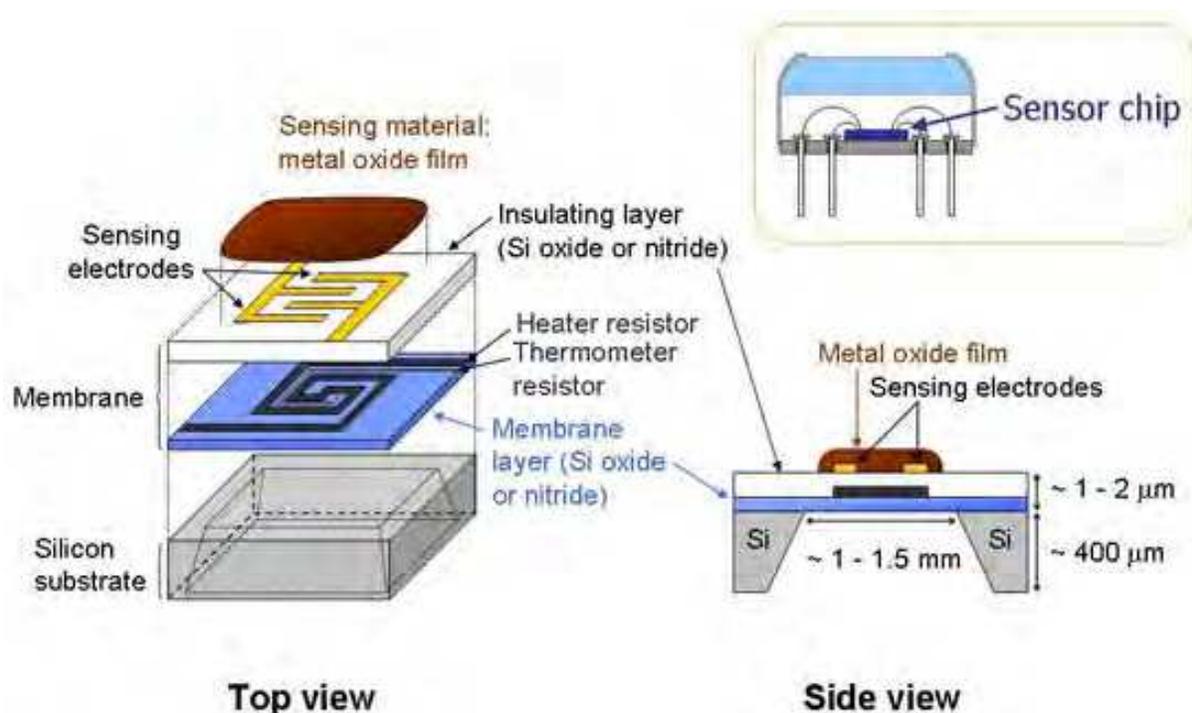


Fig. 4.2 A schematic picture of modern resistive semiconductor gas sensor (Aalto University, Research Group Gas sensors).

This kind of response of electrical conductivity to humidity changes has been extensively investigated for application as humidity sensors. As the response is related to surface adsorption, humidity sensors made using such materials generally exhibit fast response. However, the electronic conductivity can also be influenced by other gaseous species as H_2 , CO , to name a few, which can be adsorbed along with H_2O . As a result, there can be significant interference from other species, and such sensors do not exhibit the selectivity required of a practical sensor (Wang and Virkar, 2004).

Gas sensors as shown in Fig.4.2, are mostly n-type semiconductors. They detect reducing gases in air e.g leak detection in gas pipelines, indication of petrol vapour in filling stations or for alcohol tests in exhaled air. The working temperature of sensors are 200-600°C. The

grains of the sintered body are covered by adsorbed oxygen. It withdraws electrons from the bulk, forming O^{2-} ions at the surface. Charge carrier concentration in the grain volume decreases, potential barrier is formed at the grain boundaries. The electrical conductance is decreased by oxygen adsorption. The molecules of reducing gas interact with adsorbed oxygen lowering potential barrier, increasing conductance of the sensor as follows



Numerous reducing gases like hydrogen, methane, CO, ethanol vapor, H_2S can be determined in air (Gründler, 2007).

For humidity sensing, ceramic materials have mainly been used in the form of porous sintered bodies. Thus, controlling porosity and surface activity is of great importance in determining the humidity-sensitive electrical properties of ceramic products (Kim and Gong, 2005).

4.1 Barium titanate as humidity/gas sensor

Ceramic humidity sensors can be classified into the semiconducting and protonic (or ionic) type according to their conduction mechanism. The semiconducting type humidity sensor, operating at elevated temperature (300-400°C), was known to exchange charge carriers (e^- and h^+) between the adsorbed water molecule and ceramic body. While the protonic humidity sensor, usually operating at room temperature, employs protonic (H^+) conduction on the surface of the sample as a sensing mechanism. Both sensors require porous ceramic body for the adsorption of water molecule (Hwang and Choi, 1997).

To make an improved humidity sensor, the microstructure and electrical conductivity of the material should properly be controlled. In general, ceramic humidity sensors are made to be porous and electrically resistive. In this respect, $BaTiO_3$, as a protonic ceramic humidity sensor, has advantage in establishing the microstructure-property relation since the microstructure and conductivity of $BaTiO_3$ can be easily controlled by varying the amount of donor dopant such as La and the processing conditions (Hwang and Choi, 1997).

Ceramic sensors are based on the adsorption of water molecules in the pores, and variations of the structure of the adsorbed layer, as a function of humidity. The sensing mechanism of barium titanate ceramic humidity sensors at room temperature can be explained using ionic conduction model. When few water molecules are available at low humidity, they chemisorb on grain surfaces of the ceramic to form hydroxyl groups as surface charge carriers. When initial water molecules are adsorbed, each water molecule is hydrogen-bonded to two hydroxyls, and the dominant surface charge carriers will be H_3O^+ . When still more water is adsorbed, clustering of the water molecules takes place, forming a liquid-like multilayer film of hydrogen-bonded water molecules, where each water molecule is only singly bonded to a hydroxyl group. Since dissociation of H_3O^+ into H_2O and H^+ is energetically favorable in liquid water, the dominant charge carrier in high moisture environment is H^+ . These processes result in progressively decreasing impedance of barium titanate ceramic when exposed to increasing humidity (Yuk and Troczynski, 2003).

Nanocrystalline $BaTiO_3$ material has better humidity sensing properties than ceramic $BaTiO_3$, such as lower resistance and high sensitivity. However, from the application point

of view, one needs to further reduce the resistance of the resistive humidity sensor from 10^6 to 10^3 , to minimize the humidity hysteresis and to increase the sensitivity and repeatability (Wang, 2000).

Since water is a polar molecule, the negatively charged oxygen is electrostatically attached to the positively charged Ba^{2+} ions of the sensor material. The initial monolayer is chemisorbed due to the formation of a chemical bond under the influence of high electrostatic field between Ba^{2+} and oxygen of the water layer. This layer, once formed, is not further affected by exposure to humidity. The irreversible reaction for the first layer can be given as



Once the first layer is formed, subsequent layers of water molecules are physically adsorbed. This physically adsorbed water molecules dissociate because of the high electric fields in the chemisorbed water layer as given below:



The charge transport occurs when H_3O^+ ions release a proton to neighbouring water molecules which accepts it while releasing another proton and so on. This is known as Grothuss's chain reaction (Agarwal and Sharma, 2002).

5. Porous ceramics

Porous ceramics find nowadays a large variety of applications in several devices like filters, acoustic absorbers, catalytic components, selective membranes, humidity sensors, among others. There are two main kinds of porous ceramics: reticulate ceramics and foam ceramics. The former consists of interconnected voids surrounded by a web of ceramic; the latter has closed voids within a continuous ceramic matrix. Various chemical routes, besides the conventional solid state reaction route, have been developed for obtaining porous ceramics without the use of additives to avoid unwanted impurities in the final ceramic piece. An attractive alternative route, due to its simplicity and low cost, is the polymeric precursor technique based on the Pechini's patent, that results in sinteractive homogeneous powders. Solid state sintering usually results in polycrystalline bodies with pores in the 100–1000 nm range. Graphite has also been used successfully for increasing pore volume in ceramics. In conventional ceramic sintering, by heating pressed powders, a porous network is usually formed in the spaces between the particles necks, porous stability being achieved by controlling the size of the particles. An easy way of controlling pore sizes during solid state sintering is to control particle sizes of the mixing powders as well as the sintering temperature and time. A previous dilatometric analysis enables one to choose the suitable sintering temperature and time (Cosentino, 2003).

5.1 The definition of porosity and porosity of ceramics

The ceramics are made up of ionic and covalent crystals. However, real crystals are not perfect but contain imperfections that are classified according to their geometry and shape. Vacancy is an example of point defect, dislocation is a line defect, grain boundary is a planar defect (Barsoum 1997). Pores are important features for the ceramics because powder

metallurgy methods i.e mixing, milling, shaping and sintering, always result in some amount of porosity. Fig.5.1 indicates atomic mechanisms occurring during sintering. The macroscopic driving force operative during sintering is the reduction of the excess energy associated with surfaces. This can happen by (1) reduction of the total surface area by an increase in the average size of the particles, which leads to coarsening and/or the elimination of solid/vapor interfaces and the creation of grain boundary area, followed by grain growth, which leads to densification (Barsoum 1997).

Pores are three dimensional or volume defects along with cracks, precipitates and particles. Pores generally contain some gas inside them. The reason for this is the employment of an sintering atmosphere during processing. However, it is regarded as a vacuum for simplicity. Pores might be present inside the matrix phase i.e isolated pores and surfaces or they might be located at the grain boundaries and grain junctions.

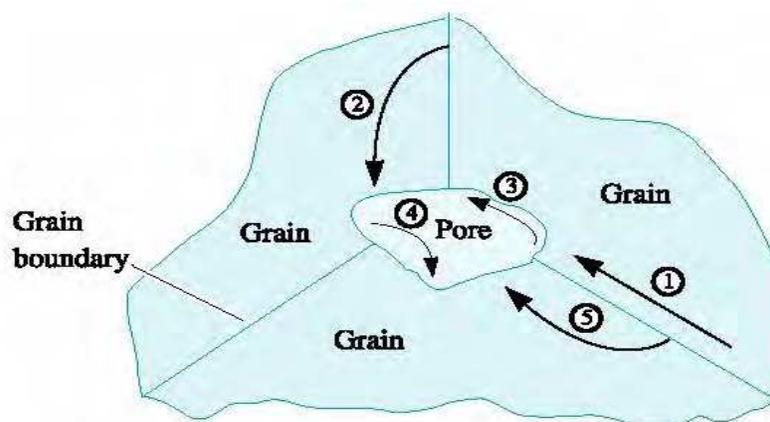


Fig. 5.1 Different diffusion mechanisms involved in sintering. The grain boundary and bulk diffusion (1, 2 and 5) to the neck contribute to densification. Evaporation-condensation (4) and surface diffusion (3) do not contribute to densification (Chiang 1997).

Three quantities relating to pores are important; the size of the pores, distribution of porosity and total amount of porosity. The shape of the pores is less important. By knowing the constituent phases of the ceramic, theoretical and actual densities can be used to obtain porosity. Mercury intrusion porosimetry can be used to determine pore size and porosity distribution (Carter 2007).

Pores are usually quite deleterious to the strength of ceramics not only because they reduce the cross-sectional area over which the load is applied, but more importantly because they act as stress concentrators (Barsoum 1997). First, they produce stress concentrations. Once the stress reaches a critical level, a crack will form and propagate. Because ceramics possess no plastic-deformation, once a crack is initiated (started), it propagates (grows) until fracture occurs. Second, pores (i.e., their size, shape, and amount) reduce the strength of ceramics because they reduce the cross-sectional areas over which a load can be applied and, consequently, lower the stress that these materials can support (Jacobs 2001).

Porosity can be converted from the density of the ceramics, measured by Archimedes' principle. The density can be calculated from the weight determinations as follows:

$$\rho = \{m_0 / [m_1 - (m_2 - m_w)]\} \times \rho_{\text{water}} \quad (5-1)$$

where m_0 is the dry weight of the samples, m_1 is the weight after dipping into water for 4h. and fluid impregnation and m_2 is the weight while immersed in water. m_w is the weight of the wire used to suspend the samples in water, which is also measured in water. All weights are in grams. ρ_{water} is the density of water (in g cm^{-3}), which is $\rho_{\text{water}} = 1.0017 - 0.0002315T$ with T is water temperature in $^{\circ}\text{C}$. The theoretical density of BaTiO_3 is considered to be 6.0 g cm^{-3} (Zhang, 2004).

5.2 Different kinds of pore-forming agents for porous BaTiO_3 fabrication

PTCR applications

Porous semiconducting BaTiO_3 can be prepared by the thermal decomposition of barium titanyl oxalate $\text{BaTiO}(\text{C}_2\text{O}_4)_2 \cdot 4\text{H}_2\text{O}$ or by the incorporation of graphite, polyvinylalcohol (PVA), polyvinylbutyral (PVB), borides, silicides, carbides, partially oxidized Ti powders and potato-starch to BaTiO_3 . These BaTiO_3 ceramics indicate large PTCR effects. Oxygen can be adsorbed at the grain boundaries due to the presence of pores. Porous ceramics are more favorable to the formation surface of acceptor states compared to dense ceramics. Porous thermistors show better heat resistance than dense ones and thus can be used as overcurrent protectors in electric circuits. (Kim, 2002, 2003)

For PTCR applications, among these agents polymers, different kinds of starch and metallic additives can be employed. The polymer additives include polyvinylalcohol (PVA), polyvinylbutyral (PVB) and (PEG). The starch can be in the sort of potato or corn starch. Partially oxidized titanium can be another choice to enhance porosity. Carbon addition can also result in the porosity increase. For humidity sensing applications, graphite and PMMA additions can be made to enhance porosity. The effects of different groups of PFAs on the grain size, porosity, PTCR and sensing property of barium titanate ceramics will be mentioned in the following paragraphs. Some of the examples of PFAs are given below, the detailed data on all the PFAs will be presented in the following paragraphs.

5.2.1 The effect of PEG on PTCR properties

Polyethylene glycol (PEG) with amount ranging from 1 to 20 wt.% was added to BaTiO_3 . The porosity and the grain size as shown in Fig. 5.2, of the n- BaTiO_3 ceramic containing 5 wt.% PEG is 10.4 % and $6.3 \mu\text{m}$, respectively, while it is 25.2 % and $5.0 \mu\text{m}$, respectively for the sample containing 20 wt.% of PEG. The crystalline structure of the n- BaTiO_3 ceramics at room temperature was tetragonal and independent on the PEG content. PTCR jump of BaTiO_3 ceramics containing 1 and 20 wt.% of PEG was measured to be 2.84×10^5 and 6.76×10^5 , respectively as shown in Fig.5.3 (Kim, 2004).

5.2.2 The effect of starch based agents on PTCR properties

The potato-starch is another pore-former used in the production of BaTiO_3 ceramics. 1-20 wt.% of potato-starch was employed to fabricate porous microstructure. The maximum porosity and minimum grain size was obtained for the sample containing 20 wt.% of potato-starch, which were 37.2% and $3.4 \mu\text{m}$, respectively. Pore-former increased porosity and decreased the grain sizes (Kim, 2002).

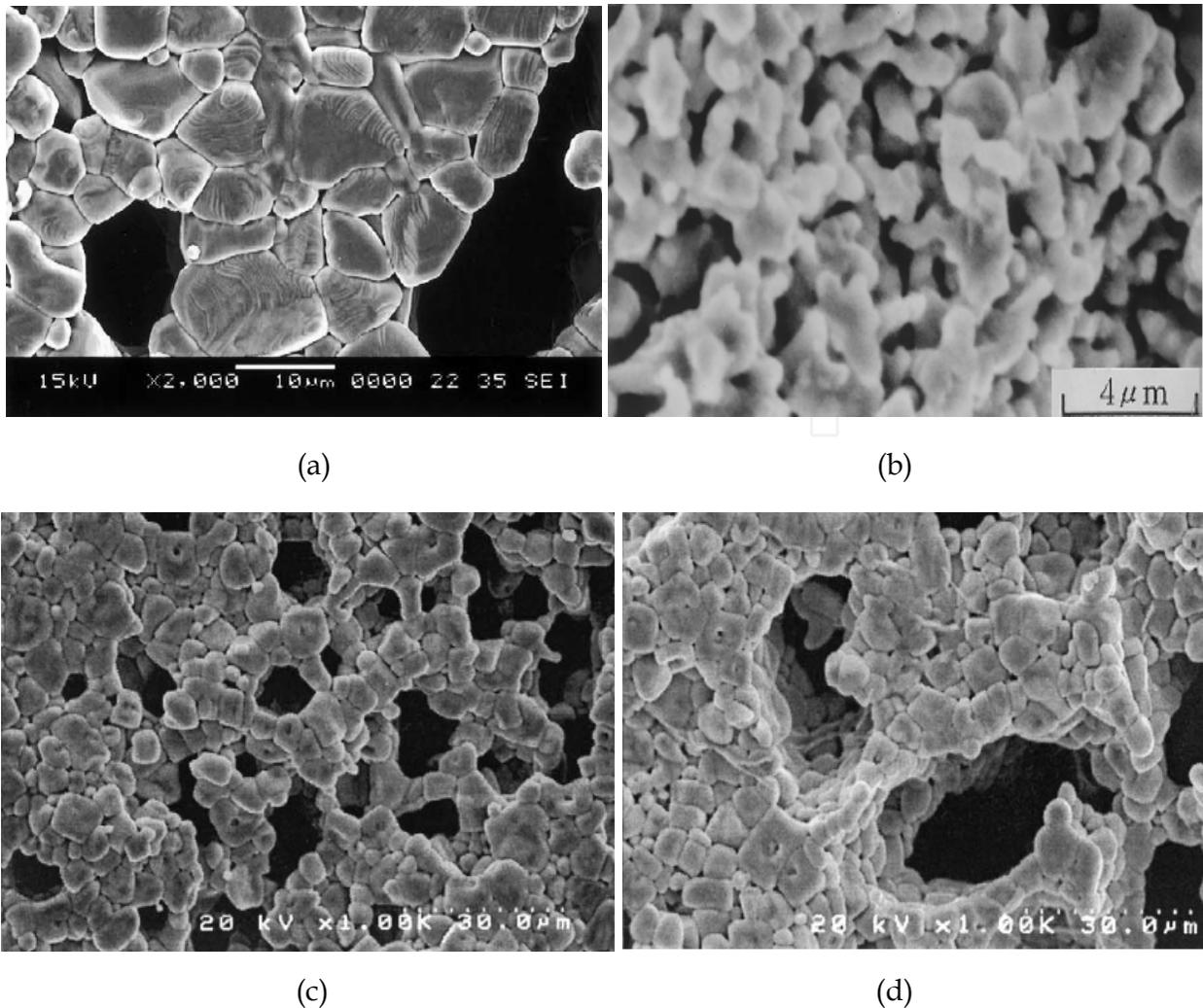
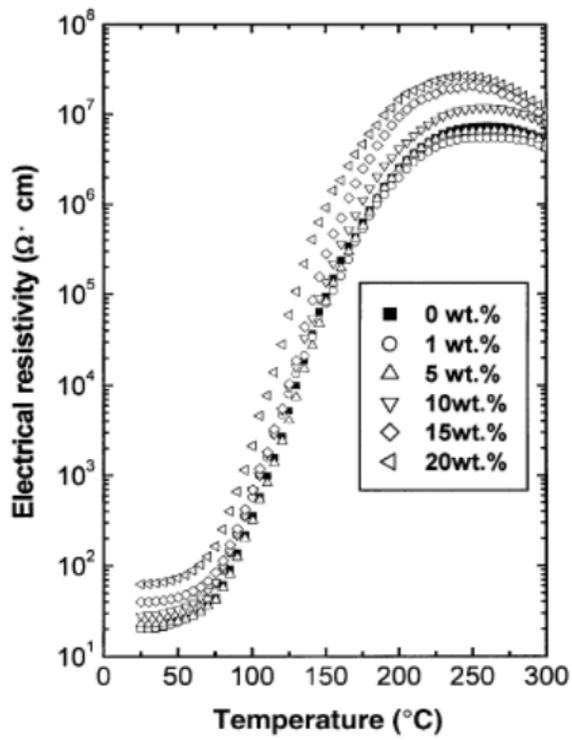


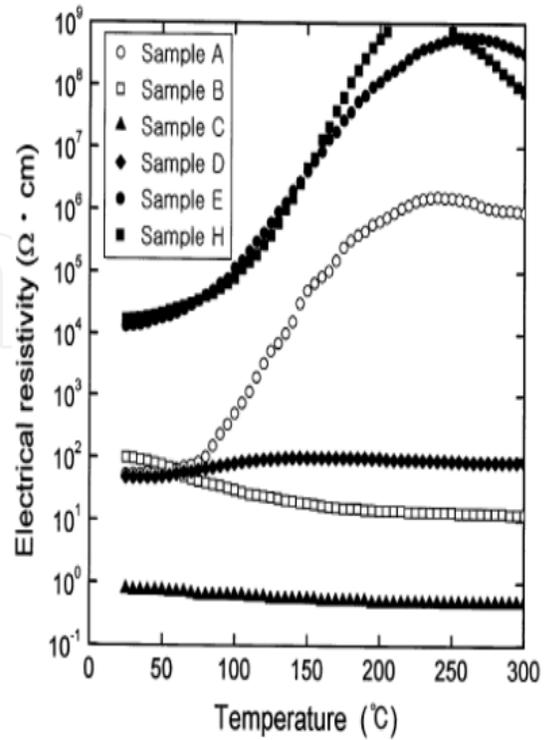
Fig. 5.2 Porous microstructures of barium titanate ceramics with the addition of (a) PEG (Kim, 2004) , (b) TiO_2 (Kim et al, , 2002), (c) corn-starch (Kim, 2002) and (d) potato-starch (Kim, 2002).

1-20 wt.% of corn-starch was added into BaTiO_3 to produce porosity. The cavities formed due to the burning-out of corn-starch during sintering act as the sites of the pore generations as shown in Fig.5.2. The maximum porosity and minimum grain size, which were 44.0% and 3.1 μm , respectively was measured for the sample containing highest amount of corn-starch. The samples containing corn-starch had a tetragonal crystal structure. The addition of corn-starch into Sb-doped BaTiO_3 ceramics results in fine microstructures (3.1-3.8 μm). The porosity and pore size increase and the grain size slightly decreases with corn-starch. The porosity increases from 7.2 to 44% with corn-starch content from 0 to 20wt.%. The grain size changed from 4.8 to 3.1 μm . These porous ceramics are advantageous to oxidize grain boundaries and to produce surface acceptor states (Kim, 2002).

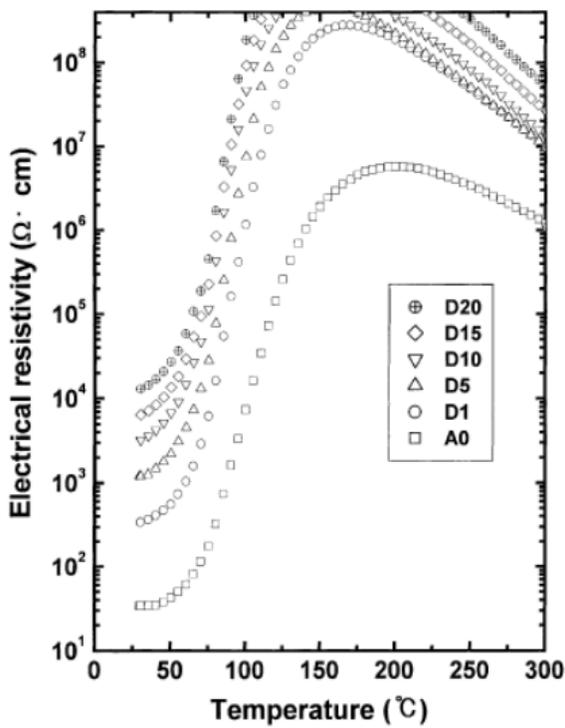
The PTCR jump of the Sb-doped BaTiO_3 ceramics with corn-starch is observed to be over 10^6 and 1-2 orders of magnitude higher than that of samples without corn-starch as given in Fig.5.3. The donor concentration i.e. Sb and grain size decrease and the electrical barrier height of grain boundaries and the porosity increase with corn-starch content. As a result, room-temperature resistivity increases with pore-forming agent content. The grain



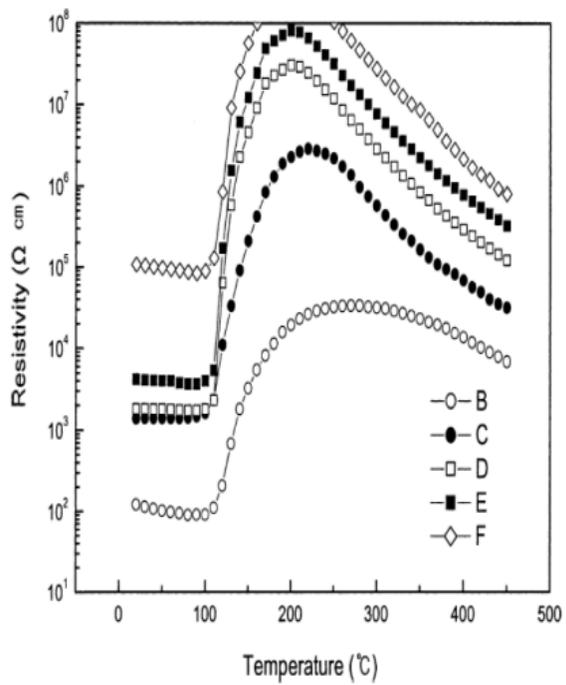
(a)



(b)



(c)



(d)

Fig. 5.3 PTCR properties of barium titanate ceramics with the addition of (a) PEG (Kim, 2004), (b) TiO_2 (Kim et al., 2002), (c) potato-starch (Kim, 2002) and (d) graphite (Park, 2004).

boundary resistivity contributes largely to the total resistivity. The electrical resistivity of grain boundaries significantly depends on the porosity. It can be deduced from this study that, adsorption of chemically adsorbed oxygen atoms at the grain-boundaries increases potential barrier height. Thus electrical resistivity of grain boundaries increases contributing to total resistivity and resulting in a PTCR effect (Kim, 2002).

The electrical resistivities of Sb doped BaTiO₃ ceramics were measured during heating under different atmospheres. The high-temperature resistivity under O₂ was higher than that under both air and reducing atmospheres of N₂ and H₂. The low resistivities obtained at high temperatures in reducing atmospheres were due to desorption of chemisorbed oxygen at the grain boundaries, decreasing potential barrier height. Besides, N₂ and H₂ gases diffuse along the grain boundaries and react with chemisorbed oxygen atoms thus chemisorbed oxygen is consumed and conduction electrons are released. This leads to a decrease in potential barrier and as a result, PTCR effects were degraded.

The room-temperature resistivity of porous samples increased with corn-starch content. The room-temperature and high temperature (above Curie temperature) resistivity values were measured to be 1.37×10^2 and 1.52×10^8 Ωcm, respectively for the sample containing 1 wt.% of corn-starch. For the rest of the samples, high-temperature resistivities were well above 10⁸ ohmcm. Besides, the resistivities of the grain boundaries increased with increasing temperature. The room-temperature and high-temperature resistivities were measured to be 3.52×10^2 and 2.79×10^8 Ωcm for the sample containing 1 wt.% of potato-starch. PTCR jump was determined to be 7.93×10^5 for the same composition. The grain boundary resistivity jump was 1.22×10^3 for this sample (Kim, 2002).

5.2.3 The effect of graphite agents on PTCR properties

0.3-2.0 mol of C (as graphite powder) was added to Sb doped BaTiO₃ to produce porous ceramics. As-sintered samples indicated tetragonal perovskite crystal structure, irrespective of the added graphite content. The porosity of the ceramics increased with graphite addition by an enhanced evolution of CO and CO₂ gases associated with the exothermic reactions. The highest porosity was determined to be 18.3%. The grain growth occurred during sintering due to exothermic reactions and maximum grain size obtained was 160.7 μm. However, as the graphite content increased, the grain sizes decreased. This is because the existing graphites act as barriers to inhibit the grain growth during sintering, reducing the grain size (Park, 2004).

The addition of graphite into BaTiO₃ substantially improved PTCR characteristics. For the sample containing highest graphite, the maximum resistivity above Curie temperature was measured to be above 10⁸ Ωcm and PTCR jump was above 1.2×10^3 . The maximum room-temperature resistivity was measured for this sample, which was 1.35×10^4 Ωcm and PTCR jump was 5.86×10^3 . The magnitude of the PTCR effect of samples containing graphite increased by 1-2 orders compared to the sample without porosifier as shown in Fig. 5.3. For the porous samples, fast response to overcurrent (below 20s) was achieved (Park, 2004).

5.2.4 The effect of metallic agents on PTCR properties

Partially oxidized Ti powders were used as pore-former in a study of Kim, Cho and Park. Ti powders were heated at 600°C for 1h in flowing oxygen gas and were covered with TiO₂.

TiO₂(Ti) powders with various contents (0-9 vol%) were added to (Ba,Sr)TiO₃ in vacuum. Vacuum-sintered ceramics were exposed to paste-baking treatment in air in order to make oxygen adsorption possible at the grain boundaries. The porosity increased and grain size decreased by the addition of TiO₂(Ti) powders. The interfaces between TiO₂(Ti) powder of a large size and BaTiO₃ powder of a small size provide the sites of the pore generations, resulting in porosity increase. 46.0% and 1.0µm are the porosity and grain size values, respectively for the sample containing 9 vol% of TiO₂(Ti). Small grain size may be due to a decrease in the driving force for the grain boundary movement with TiO₂(Ti) addition. TiO₂(Ti) addition and vacuum sintering (low oxygen content and small grain size) transformed the tetragonal crystal structure of BaTiO₃ to cubic. (Ba,Sr)TiO₃ ceramics containing 5 vol% of TiO₂(Ti) showed excellent PTCR characteristic, i.e. low room-temperature resistivity ($1.8 \times 10^{12} \Omega\text{cm}$) and the high ratio of maximum resistivity to minimum resistivity (1.5×10^{16}) as shown in Fig. 5.3 (Kim et al., 2002).

Humidity/Gas sensing Applications

5.2.5 The effect of graphite agents on humidity sensing

The effect of graphite addition on grain size, porosity and humidity sensing properties was investigated. Four different graphite containing compositions (C-1/C-4) were sintered at 1200-1500°C for 2-6h.

The graphite addition increased the grain size of the donor doped samples due to heat generated by the exothermic reactions of carbon combustion. However, the grain size decreased by further addition of graphite powder, because of the graphite segregation at the grain boundaries (Ertug et al., 2005). This result is in good agreement with (Park, 2004)'s study on PTCR properties.

The addition of graphite resulted in a porous microstructure as shown in Fig.5.4. The maximum grain size was measured for the sample (BTLC-1) sintered at 1500°C for 6h. and it was 15.7 µm. Upon sintering at 1500°C for 6h., the grain size of BTLC-4 composition reached 13.3 µm. The grain size decreased drastically when the sintering temperature was decreased from 1500°C to 1200°C for 2-6h. For the sample sintered at 1200°C for 6h., the grain size was measured to be 5.7 and 5 µm for BTLC-1 and BTLC-4 compositions, respectively (Ertug et al., 2005).

The porosity percentage of the graphite containing compositions changed dramatically when the sintering temperature was increased from 1200 to 1500°C. The porosity change was slight between 1200-1400°C however after sintering at 1500°C, most of the porosity in the microstructure was eliminated and dense samples were obtained (Ertug et al., 2005).

The minimum porosity percentage was measured for the sample (BTLC-1) sintered at 1500°C for 6h. and it was 12 %. When graphite addition was increased from 3.5 to 6.5%, the porosity percentage changed from 59 to 64.9 % upon sintering at 1200°C for 6h (Ertug et al., 2005).

The humidity sensing properties of graphite containing compositions were given in Fig.5.5 and 5.6. The transfer function of the humidity sensitive samples, which were sintered at 1200°C was of exponential type. At the low humidity percentages, the electrical resistance decreased with relative humidity linearly. When the relative humidity increased beyond the

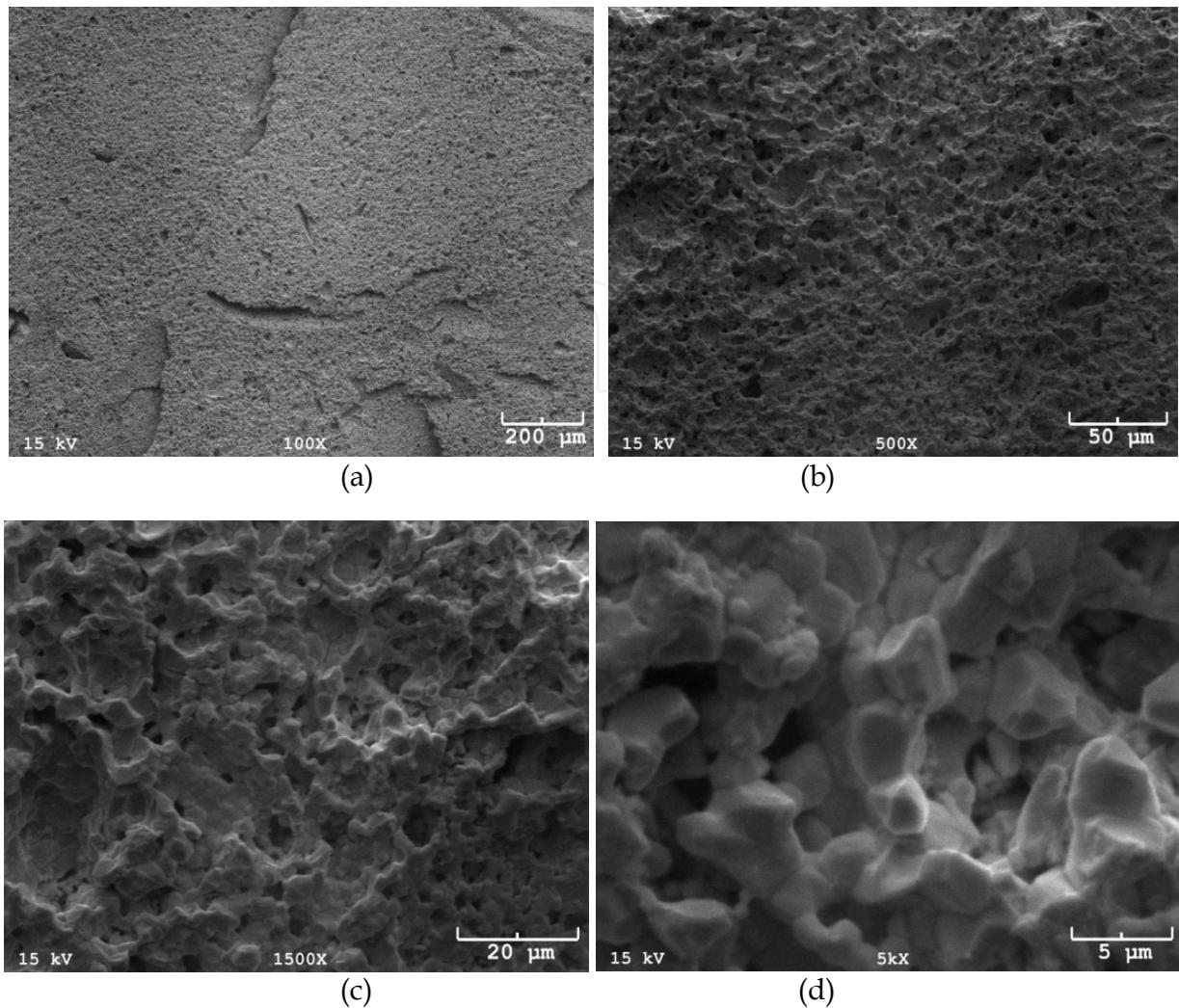


Fig. 5.4 The porous microstructures of graphite containing barium titanate samples (Ertug, 2008).

critical value, the electrical resistance-relative humidity curve became exponential. The minimum electrical resistance was measured for the samples which contain higher porosity percentages. When the content of the graphite was increased, the transfer function of the humidity sensitive sample did not change, i.e exponential curve. However, the electrical resistance values indicated a slight decrease due to higher porosity percentage (Ertug, 2008).

When the samples were sintered at 1500°C, porosity percentages decreased by a great amount. As shown in Fig.5.6, as-sintered samples did not exhibit a change in the electrical resistance with relative humidity (Ertug, 2008).

5.2.6 The effect of PMMA agent on humidity sensing

The three different barium titanate compositions containing PMMA as pore forming agent were investigated. The samples were sintered at 1200-1500°C for 2-6h. The grain size of the samples decreased with PMMA content. The maximum grain size was measured for the sample sintered at 1500°C for 6h. and it was 14.87 μm. The maximum porosity was determined for the sample containing maximum PMMA amount, which was 53.5 % (Ertug, 2006).

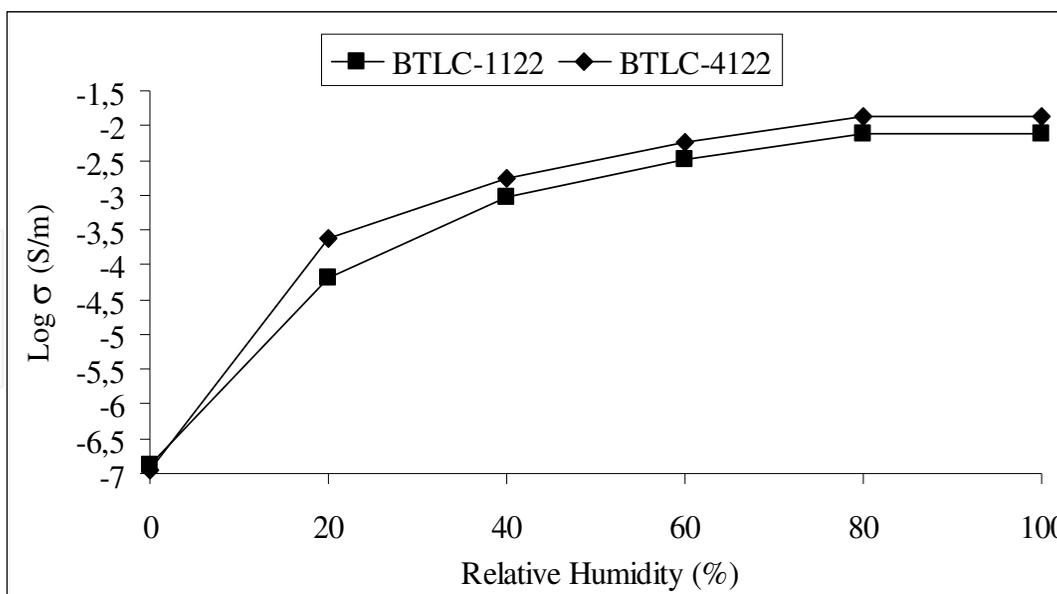


Fig. 5.5 The humidity sensing property of graphite containing samples sintered at 1200°C (Ertug, 2008).

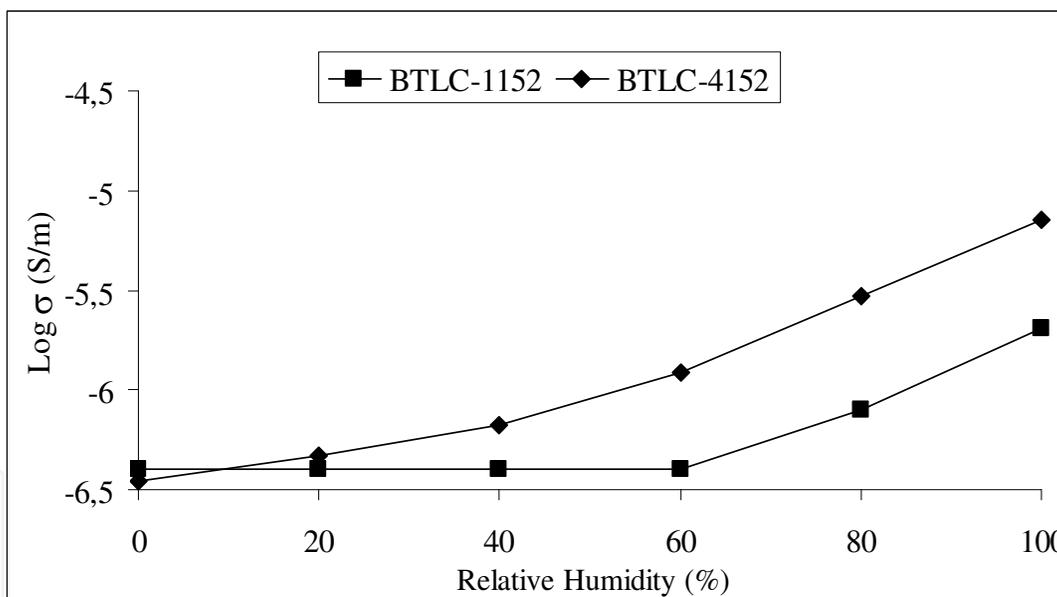


Fig. 5.6 The humidity sensing property of graphite containing samples sintered at 1500°C (Ertug, 2008).

The transfer functions of the barium titanate samples changed with sintering temperature. When the samples were sintered at 1200°C, the transfer function was exponential. However, when the sintering temperature was increased to 1500°C, the transfer function of the composition containing lower PMMA, included a dead band region where at low relative humidity, the electrical resistance remained constant with humidity. The dead band region was valid up to 40% of relative humidity. As shown in Fig.5.7., the composition which contained higher amount of PMMA, did not show a certain dead band region (Ertug, 2008).

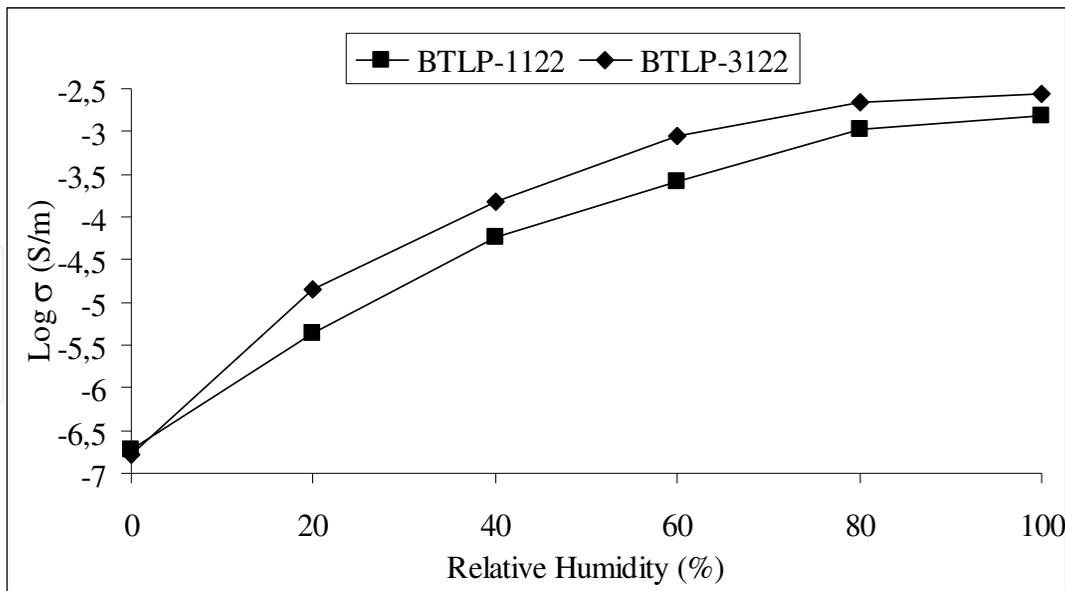


Fig. 5.7 The humidity sensing property of PMMA containing samples sintered at 1200°C (Ertug, 2008).

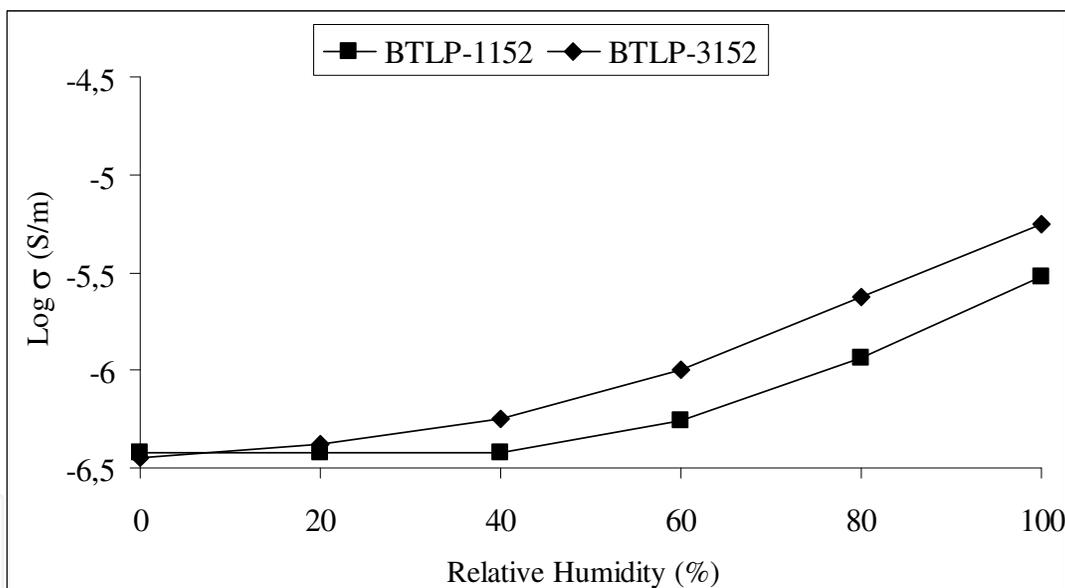


Fig. 5.8 The humidity sensing property of PMMA containing samples sintered at 1500°C (Ertug, 2008).

However, the electrical resistance did not change very much with relative humidity up to 40% of relative humidity. A clear drop in the electrical resistance was observed only after 60% of relative humidity (Ertug, 2008).

6. Conclusion

n-type semiconducting barium titanate ceramics have applications as thermistors and sensors. For barium titanate in order to exhibit PTCR and gas (or humidity) sensing property, first donor doping by trivalent or pentavalent cations is necessary. The

improvement of porosity is another requirement for PTCR and sensor applications. Porous barium titanate ceramics are generally fabricated using different kinds of pore-forming agents (PFAs). The fabrication process is carried out using powder metallurgy methods namely mixing with PFAs, shaping and sintering. PFAs, which are used for porous barium titanate fabrication, can be grouped into several categories depending on the type of the pore-former. Polymeric agents, metallic agents, starch-based agents and carbon-based agents. An additional binder burn out step is employed for some of the pore-formers such as PEG and direct sintering is done for other pore-formers such as starch and graphite. The pore-forming mechanisms of several PFAs are different from each other. When oxidized Ti powders are used as PFAs, the difference in the powder size of TiO_2 (18 μm) and BaTiO_3 (1 μm) powders lead to pore generation. However, gas evolution during the burning of carbon results in porosity when graphite PFA is used. When polymeric agents are used to produce porosity, organic components are pyrolyzed upon binder removal process. The porosity improvement by PFAs lead to humidity or reducing gas sensitivity of barium titanate based ceramics. Besides, the oxidation of the grain boundaries are enhanced by porosity increase which in turn improves PTCR property. Brand new PFAs such as several polymeric agents, can be used to produce porous barium titanate or known to be effective PFAs can be applied to it in order to produce more sensitive sensors or to obtain more pronounced PTCR effect in BaTiO_3 . The effect of PFAs on the porosity (and pore size) and grain size of barium titanate ceramics and also the different pore-forming mechanisms of PFAs are currently open to further investigation since this particular area is based on trial and error method.

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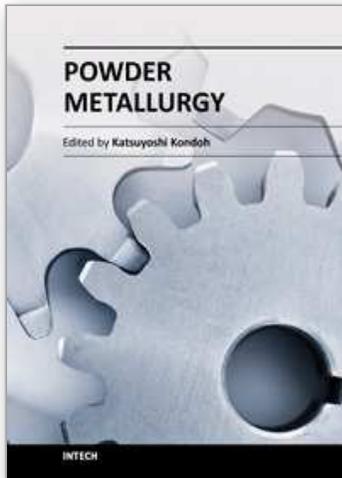
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From high-performance, economical and environmental points of view, Powder metallurgy process shows remarkable advantages in production of parts and components due to their special compositions by elemental mixing and 3-dimensional near net shape forming methods. Powder metallurgy process can be applied to not only metal materials but also ceramics and organic materials, which both are employed as structural and electrical products. Author contributions to Powder metallurgy present excellent and significantly important research topics to evaluate various properties and performance of P/M materials for applying these materials as actual components. In particular, the life estimation of P/M ferrous materials by sliding contact fatigue test and tribological performance evaluation of P/M semi-metallic materials are focused and introduced in this book.

How to reference

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