

CHAPTER 2

RELATED THEORY

2.1 Solid Solutions

Solid solution involves the ability of one atom or group of atoms to substitute into the crystal structure of another atom or group of atoms without resulting in a mixture of structures. In a solid solution only one crystallographic structure is detectable. Solid solution must be distinguished from mixtures. In a mixture two or more components are present, but they retain their own identity and crystal structure. Solid solution does not have to be complete between two different components and generally is not. The limits are determined by the similarity in the crystal structures and the size of ions or atoms.

If a material crystallizes in the presence of foreign atoms, they may be almost completely rejected by crystal if they appreciably increase the energy of the crystalline form. On the other hand, if building them into the host structure in an ordered way leads to a large lowering of the system's energy a new crystalline form develops. In intermediate cases foreign atoms fit into the structure in random way as the crystal is built up. When this occurs, there is usually a change in the cell size with composition in accordance with *Vegard's law* [6] that the lattice-cell dimensions vary linearly with the concentration of solute added.

A solid solution is basically a crystalline phase that can have variable composition. As with doped crystals, simple solid solutions are one of two types: in

substitutional solid solutions, the atom or ion that is being introduced directly replaces an atom or ion of the same charge in the parent structure; in interstitial solid solutions, the introduced species occupies a site that is normally empty and no ions or atoms are left out.

2.1.1 Substitutional Solid Solutions

Substitution of one ion for another is common in the formation of ceramic crystal. However, in most systems only a limited number of foreign atoms can be added to the substitutional solid solution, an excess above the solubility limit at a given temperature results in the formation of a second phase.

There are several factors determining the extent substitution that can take place in solid solutions, and a number of rules expressing these factors have been devised. Factors which allow extensive substitution are as follows.

1. Size Factor: If the sizes of two ions differ by less than about 15% conditions are favorable for the formation of substitutional solid solutions [7]. If the relative ion sizes differ by more than 15%, substitution is generally limited and is usually less than a fraction of 1% [7]. This factor is by far the most important for ionic compounds.

2. Valency Factor: If the added ion has a valence different from that of the host ion, substitution is limited. It can occur, but other structural changes are also required to maintain overall electrical neutrality.

3. Chemical Affinity: The greater the chemical reactivity of the two crystalline materials, the more restricted is solid solubility, since a new phase is usually more stable. For oxides this restriction is usually implicit in factors of ion valency and size.

4. Structure Type: For complete solid solubility the two end members must have the same type of crystal structure. For example, TiO_2 could obviously not form a complete series of solid solutions with SiO_2 [7]. However, restrict limited solid solution.

On the basis of these factors, an estimate of the extent of substitutional solid solution to be expected can usually be obtained. For oxides, the major factors are the relative ion sizes and valencies. Although different ion sizes definitely precluded extensive solid-solution formation, valence differences can frequently be made up in other ways.

The effect of substituents is a complex matter but, with caution, a number of important generalizations can be made regarding heterovalent substituents in perovskite (ABO_3). Donor dopants, i.e. those of higher charge than that of the ions they replace, are compensated by cation vacancies; acceptors, i.e. dopants of lower charge than that of the replaced ions, are oxygen vacancies. Each dopants type tends to suppress the vacancy type that the other promotes. The common dopants in perovskite-type ceramics are listed in TABLE 2.1.

TABLE 2.1 Common heterovalent substituents. [8]

A-site donors	La^{3+} , Bi^{3+} , Nd^{3+}
B-site donors	Nb^{5+} , Ta^{5+} , Sb^{5+}
A-site acceptors	K^+ , Rb^+
B-site acceptors	Co^{3+} , Fe^{3+} , Sc^{3+} , Ga^{3+} , Cr^{3+} , Mn^{3+} , Mn^{2+} , Mg^{2+} , Cu^{2+}

Solid solutions can be of two broad types: those involving homovalent substitution and those involving heterovalent or aliovalent substitution. In homovalent substitution, ions are substituted by other ions of the same charge, and no additional changes are needed to retain charge balance. In heterovalent solid solutions, ions are substituted by other ions of different charge. Consequently, additional changes involving creation of vacancies or interstitials (ionic compensation) or electrons or holes (electronic compensation) are needed [6]. For ionic compensation, there are four possibilities for cation substitution, summarized in Figure 2.1.

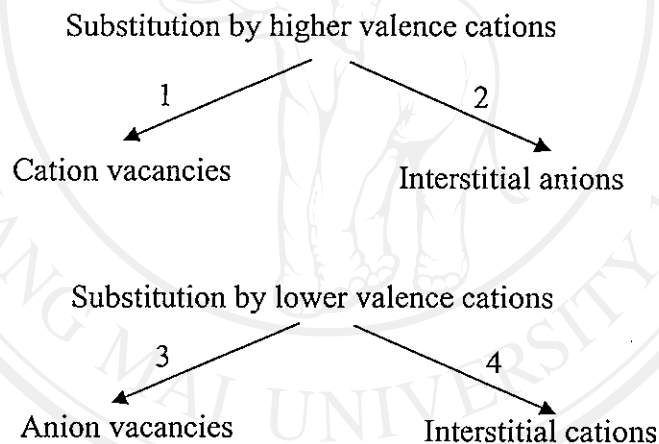


Figure 2.1 Solid solution mechanisms involving substitution of heterovalent cations [6].

All mechanism can be explained the following:

Ionic Compensation Mechanisms [6]

1. Creating cation vacancies

If the replaceable cation of the host structure has lower charge than that of the cation which replaces it, additional changes are needed to preserve

electroneutrality. One way is to create cation vacancies by leaving out more cations of the host structure.

2. Creating interstitial anions

The other mechanism by which a cation of higher charge may substitute for one of lower charge is to create, at the same time, interstitial anions. This mechanism is not common because most structures do not have interstitial sites large enough to accommodate extra anions.

3. Creating anion vacancies

If the replaceable ion of the host structure has higher charge than that of the replacing cation, charge balance may be maintained by creating either anion vacancies or interstitial cations. However, interstitial cations can happen but only small replacing cations.

4. Creating interstitial cations

This is a common solid solution mechanism provided the host structure has suitable-sized interstitial sites to accommodate the extra cations. Interstitial cation mechanism is possible to occur with acceptor substitution at the same time and too small cations are needed to enter interstitial holes.

2.1.2 Interstitial Solid Solutions

If added atoms are small, they can go on interstitial sites in the crystal to form solid solutions. This type of solution is particularly common with metallic bonding.

The ability to form interstitial solid solutions depends on the same factors, size, valency, and chemical affinity. The size effect depends on the original host crystal structure. Two types of interstitial site are tetrahedral and octahedral holes. The octahedral holes in close-packed structure are much bigger than the tetrahedral holes; the radius of holes is $0.414r$ and $0.225r$ (where r = radius of host atom), respectively. The addition of ions on interstitial sites requires some associated charge balance to maintain electrical neutrality. This can be accomplished by vacancy formation, substitution solid solution, or changes in the electronic structure. All mechanism can be shown in Figure 2.2.

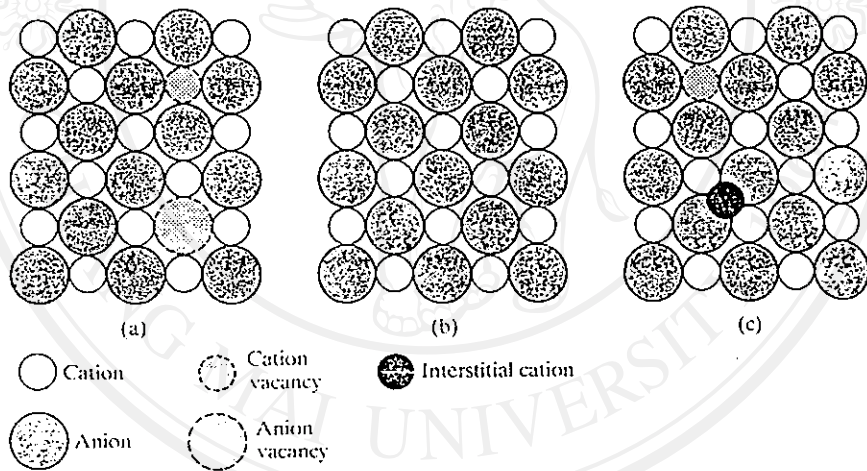


Figure 2.2 Schematic illustration of intrinsic point defects in a crystal of composition MX: (a) Anion and cation vacancy; (b) Perfect crystal; (c) Cation vacancy and Interstitial cation [9].

2.1.3 Solid Solution of BaTiO₃ Based

BaTiO₃ has the perovskite structure, as illustrated in Figure 2.3. Each barium ion is surrounded by 12 oxygen ions. The oxygen ions plus the barium ions form a face-centered cubic lattice. The titanium atoms reside in octahedral interstitial

positions surrounded by six oxygen ions. Because of the large size of the Ba ions, the octahedral interstitial position in BaTiO_3 is quite large compared to the size of the size of the Ti ions. The Ti ions are on the margin of being too small to be stable in this octahedral position. It is believed that there is minimum-energy positions off-center in the direction of each of the six oxygen ions surrounding the Ti ion. The Ti ion positions randomly in one of these six possible minimum-energy sites. This results in spontaneous polarization for each Ti ion. Since each Ti ion has a +4 charge, the degree of polarization is very high. When an electric field is applied, the titanium ions can shift from random to aligned positions and result in high bulk polarization and high dielectric constant.

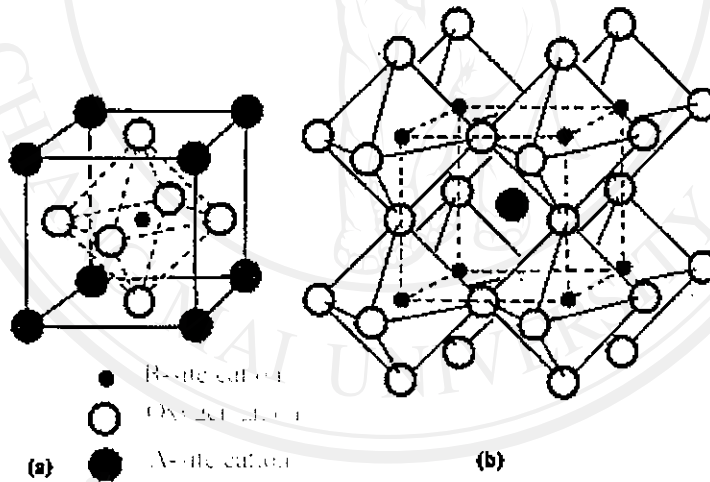


Figure 2.3 (a) Perovskite structure with B at origin and (b) with A at origin for BaTiO_3 [10].

The high dielectric constant of BaTiO_3 -type ceramics results from the crystal structure. Temperature has a strong effect on the crystal structure and polarization characteristics of BaTiO_3 as shown in Figure 2.4. Above 120°C , BaTiO_3 is cubic and the behavior described above prevails. The thermal vibration is high enough to result in the random orientation of the titanium ions. When the temperature

decreases to about 120 °C, the structure changes to tetragonal. The octahedral site is now distorted with the Ti ion in an off-center position. This results in a permanent dipole. The temperature of transformation from cubic to tetragonal and from spontaneous random polarization to permanent dipole domains is called the *Curie temperature*, T_c .

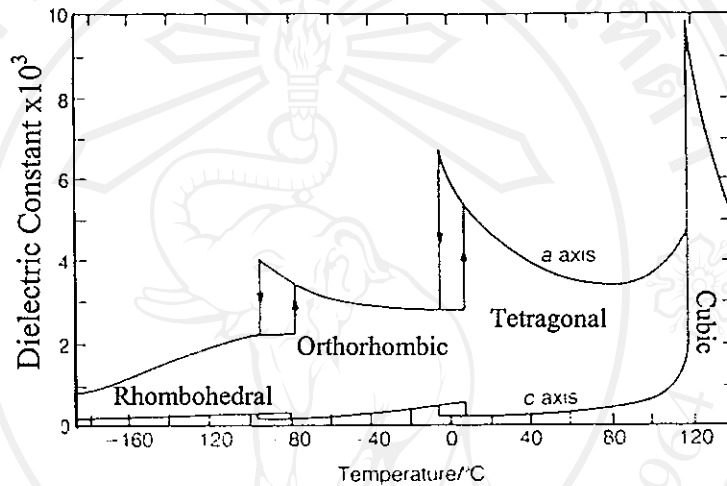


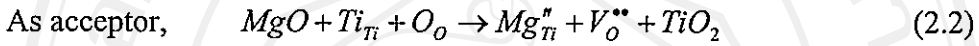
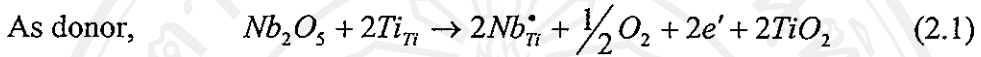
Figure 2.4 Changes in dielectric constant of BaTiO₃ as a function of temperature and crystallographic form [10].

The polarization characteristics can be modified by crystal chemical alterations of the crystal structure. Ba and Pb ions are very large and result in a large octahedral site in which the titanium ions can readily move. Substitution of smaller ions for Ba or Pb reduces the size of the octahedral site and restricts the motion of the Ti ion. Substitutions also modify the temperature effect.

In this study, double substitution by two type of dopant as acceptor, Mg²⁺ and donor, Nb⁵⁺ take place simultaneously at Ti-site. Considering the possible defects

in BT what follows, the influence of the additives on the defect concentration will be discussed. Dopant concentration leads to different charge compensation mechanisms.

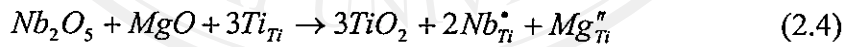
For low additive concentrations (0.05 mole percent of Nb^{5+} and 1 mole percent of Mg^{2+}), vacancies formation is limited. In these cases, an electronic compensation regime prevails for both kinds of dopants to give the formula



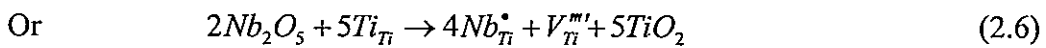
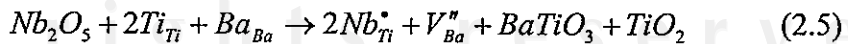
In equations (2.1) and (2.2), donor dopant, Nb^{5+} and acceptor, Mg^{2+} is in the BT lattice replacing Ti^{4+} at the same time. This phenomenon yields to oxygen vacancies trap electrons according to



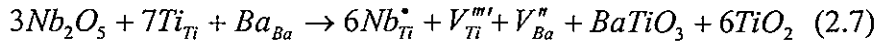
And providing that overall electroneutrality prevails at last. The possible mechanism proposed for the ionic compensation regime:



For high additives contents, the feasible mechanisms of ionic compensation can occur by create cation vacancies to preserve electroneutrality in those regions represent,



For Nb-doped BT, represent the possible mechanisms of compensation in those regions with high donor dopant contents:



where Nb_{Ti}^{\bullet} is a substitutional Nb ion on a Ti-site, net charge +1

V_{Ba}^n is a barium ion vacancy, net charge -2

$V_{Ti}^{m'}$ is a Titanium ion vacancy, net charge -4

$V_O^{\bullet\bullet}$ is a oxygen ion vacancy, net charge +2

Mg_{Ti}^n is a substitutional Mg ion on a Ti-site, net charge -2

In case of Mg^{2+} substitution, the mechanism created the $V_O^{\bullet\bullet}$ and Mg_{Ti}^n to compensate charge follow equation (2.2). The isovalent substitution of Ba^{2+} can occur with high concentration of Mg^{2+} . However, the ionic radius of Mg^{2+} is substantially smaller [11-12]. More than 15 percent different between the ionic sizes of Mg^{2+} and Ba^{2+} cations, as well as the crystallization of $MgTiO_3$ with the ilmenite-type structure (order corundum) instead of the perovskite [12-13], have been indicated as the restricting factors for the solid solubility of Mg^{2+} in the lattice.

Selection of substituents is mainly base on three factors including charge neutrality, tolerance factor and solubility. The stability of perovskite lattice is related to the high degree of ionic bonding and to the proper value of the tolerance factor, t , which defines the relation between the ionic radii in the perovskite lattice. Using the relation [6, 14]

$$t = \frac{\bar{r}_A + r_O}{\sqrt{2}(\bar{r}_B + r_O)} \quad (2.8)$$

where \bar{r}_A and \bar{r}_B are the average radii of A and B site ions, respectively and r_O is ionic radius of oxygen. The radius of cations can be show in TABLE 2.2.

TABLE 2.2 Ionic and crystal radius of some ions. [15]

Elements	Ionic radius (Å)	Co-ordination Number	Crystal radius (Å)
Ba ²⁺	1.49	12	1.60
Mg ²⁺	0.86	12	1.20
Mg ²⁺	0.86	6	0.72
Ti ⁴⁺	0.75	6	0.605
Nb ⁵⁺	0.69	6	0.57
O ²⁻	1.26	6	1.40

The reason why structural distortions occur in many perovskite is that the A and/ B atoms are not exactly the right size to fit the sites generated by the remainder of the structure. In ideal, $t=1$ is fully complete substitution. In practice, there is some flexibility over bond lengths and usually, a cubic perovskite forms with t in range $0.9 < t < 1$.

For $t > 1$, the B site is larger than required. If t is slightly greater than 1.0, the structure distorts but is still basically a perovskite as in BT, $t = 1.06$.

For $t < 0.85$, distorted perovskite structures are no longer stable and the A cation requires a smaller site. According to the above description there are several crystallochemical reasons that Nb⁵⁺ and Mg²⁺ ions prefer to substitute Ti-site in octahedral hole than that Ba²⁺ in BT lattice. The formation of solid solutions between dopants and BT at Ti-site is expected to be limited. The solubility limit of Nb⁵⁺ and Mg²⁺ can find out by XRD technique that use to detect the presence the second phase in the sample. Moreover, the second way to characterize solid solutions by XRD is to

measure powder pattern accurately and obtains the unit cell dimensions, since these may undergo a small contraction or expansion as composition varies. Usually, the unit cell expands if a small ion is replaced by a larger one, and vice versa. From Bragg's law and the *d-spacings* formulae, an increase in the unit cell parameters leads to an increase in *d-spacings* of the powder lines; the whole pattern shifts to lower values of 2θ , therefore.

According to *Vegard's law* [6], unit cell parameters should change linearly with composition. It should be noted that *Vegard's law* is often obeyed only approximately and accurate measurements reveal departures from linearity. *Vegard's law* is not really a law but rather a generalization that applies to solid solutions formed by random substitution or distribution of ions. It assumes implicitly that the changes in unit cell parameters with composition are governed purely by the relative sizes of the atoms or ions that are 'active' in the solid solution mechanism.

2.2 Theory of Sintering

Sintering can be defined as removal of the pores between starting particles accompanied by shrinkage of the component combined with growth together and formation of strong bonds between adjacent particles. The densification of a particulate ceramic compact is technically referred to as sintering. The following criteria must be met before sintering can occur:

1. A mechanism for material transport must be present.
2. A source of energy to activate and sustain this material transport must be present.

The primary mechanisms for transport are diffusion and viscous flow. Heat is the primary source of energy, in conjunction with energy gradients due to particle-particle contact and surface tension.

2.2.1 Stages of Sintering

Sintering is often thought of in stages according to the sequence in physical changes that occur as the particles bond together and the porosity disappears. The stages and primary physical changes that occur in each stage are listed in TABLE 2.3.

TABLE 2.3 Stages of Sintering. [10]

1 st Stage (initial)	Rearrangement
	Neck formation
2 nd Stage (intermediate)	Neck growth
	Grain growth
	High shrinkage
	Pore phase continuous
3 rd Stage (final)	Much grain growth
	Discontinuous pore phase
	Grain boundary pores eliminated

The initial stage involves rearrangement of particles and initial neck formation at the contact point between each particle. The rearrangement consists of slight movement or rotation of adjacent particles to increase the number of points of

contact. Relative density of the compact may increase due mostly to the increased packing of the particles. Bonding occurs at the points of contact where material transport can occur and where surface energy is highest. The changes that occur during the first stage of sintering are illustrated in Figure 2.5 (b).

The second stage of sintering is referred to as intermediate sintering. The physical changes that occur during second-stage sintering are illustrated in Figure 2.5 (c). The size of the necks between particles grows. Porosity decreases and the centers of the original particles move closer together. This results in shrinkage equivalent to the amount of porosity decrease. The grain boundaries begin to move so that on particle (now called a grain), begins to grow while the adjacent grain is consumed. This allows geometry changes that are necessary to accommodate further neck growth and removal of porosity. Intermediate sintering continues as long as pore channels are interconnected and ends when pores become isolated. Most of the shrinkage during sintering occurs during second-stage sintering.

The third stage of sintering is referred to as final sintering. It involves the final removal of porosity. The porosity is removed by vacancy diffusion along grain boundaries. Therefore, the pores must remain close to the grain boundaries. Pore removal and vacancy diffusion are aided by movement of grain boundaries and controlled grain growth. However, if grain growth is too rapid, the grain boundaries can move faster than the pores and leave them isolated inside a grain. As the grain continues to grow, the pore becomes further separated from the grain boundary and has decreased chance of being eliminated. Therefore, grain growth must be controlled to achieve maximum removal of porosity.

Grain growth is driven by surface energy. The forces of nature reduce surface area to a minimum to minimize surface free energy. That is why drops of water or mercury form into spheres. The same energy relationships exist in a solid material during sintering. Curved grain boundaries move in such a way that they gain larger radius of curvature, that is, straighten out. This can only be accommodated by growth of the grains. Smaller grains have a smaller radius of curvature and more driving energy to move, change shape, and even to be consumed by larger grains. The physical changes that occur during the final stage of sintering are illustrated in Figure 2.5 (d).

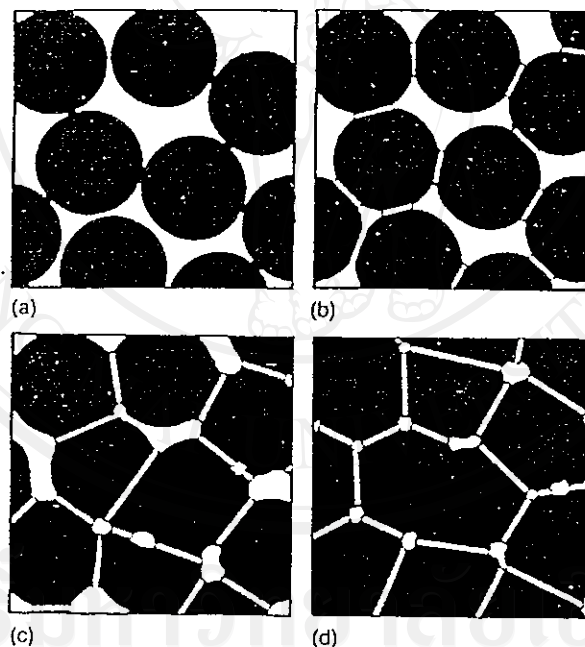


Figure 2.5 Development of the ceramic microstructure during sintering: (a) loose powder particles, (b) initial stage, (c) intermediate stage and (d) final stage [16].

Sintering can occur by a variety of mechanisms, as summarized in TABLE 2.4. Each mechanism can work alone or in combination with other mechanisms to achieve densification.

TABLE 2.4 Sintering Mechanisms. [10]

Type of sintering	Material transport mechanism	Driving energy
Vapor-phase	Evaporation-condensation	Differences in vapor pressure
Solid-state	Diffusion	Differences in free energy or chemical potential
Liquid-phase	Viscous flow, diffusion	Capillary pressure, surface tension
Reactive liquid	Viscous flow, solution-precipitation	Capillary pressure, surface tension

In this study, we used the solid-state and liquid-phase sintering. So, solid-state and liquid-phase sintering is discussed only briefly.

2.2.2 Solid-State Sintering

Solid-state sintering involves material transport by volume diffusion. Diffusion can consist of movement of atoms or vacancies along a surface or grain boundary or through the volume of the material. In general, the solids are not raised to their melting temperatures, and so the diffusion reaction occurs in the solid state. Solid state reactions only take place at the interface of the two solids and once the surface layer has reacted, reaction can only continue as reactants diffuse from the bulk to the interface. Raising the temperature enables reaction at the interface and diffusion through the solid to proceed faster than they do at room temperatures. Volume diffusion, whether along grain boundaries or through lattice dislocations, does not result in shrinkage [10]. The driving force for solid-state sintering is the

difference in free energy or chemical potential between the free surfaces of particles and the points of contact between adjacent particles. The driving force of solid-state sintering on the particle size, indicating that particle diameter has a major effect on the rate of sintering. The smaller the particle and high temperature have the greater the rate. Due to finer-particle-size powder can be sintered more rapidly and at a lower temperature than coarser powder. Thus fine starting powders can be used since the higher the surface area of the powder the greater the driving forces for densification so that higher densities can be achieved. Another concern with solid-state sintering is exaggerated grain growth. Sometimes grains grow so rapidly that pores are trapped within the grains rather than moving along the grain boundaries until the pores are eliminated. All of the steps on going compact to a microstructure made up of bonded grains are included in the term sintering.

Despite its widespread use, the simple solid state method has several disadvantages. Firstly, high temperatures are generally required. This requires a large input of energy. In addition, the phase or compound desired may be unstable or decompose at such high temperatures. A second disadvantage is the slowness of solid state reaction. Because of this, it is important that the starting materials are ground to give a small particle size, and very well mixed to maximize the surface contact area and minimize the distance that the reactants have to diffuse. To achieve a homogeneous mix of small particles with ceramic method it is necessary to be very thorough in grinding the reactants. A third disadvantage is that the product is often not homogeneous in composition.

2.2.3 Liquid Phase Sintering

Liquid-phase sintering involves the presence of a viscous liquid at the sintering temperature and is the primary densification mechanism. Three factors control the rate of liquid-phase sintering:

1. particle size
2. viscosity
3. surface tension

The viscosity and surface tension are affected strongly by composition and temperatures. Liquid-phase sintering occurs most readily when the liquid thoroughly wets the solid particles at the sintering temperature. The liquid in the narrow channels between the particles results in substantial capillary pressure, which aids densification by several mechanism: rearranges the particles to achieve better packing, increases the contact pressure between particles, which increases the rate of material transfer by solution/precipitation, creep and plastic deformation, vapor transport, and grain growth. It should be noted that smaller particles result in higher capillary pressure and also have higher surface energy due to the small radius of curvature and thus have more driving energy for densification than coarser particles.

A significant proportion of ceramic products used in low-temperature applications are predominantly crystalline materials containing a minor amount of a glassy phase distributed in the grain boundaries. When the liquid coats each grain, the material may often be sintered to a higher density at a lower temperature with less of a tendency for exaggerated grain growth. However, differential rates of densification and grain growth may produce an inhomogeneous microstructure and a lower average density. The requirements for complete densification of a ceramic system are:

1. Enough liquid must be present at the sintering temperature.
2. The liquid must wet the solid so that very low to zero contact and dihedral angles are required.
3. The solid must be partially soluble in the liquid.

The liquid phase sintering process was characterized as having three stages of densification (Figure 2.6).

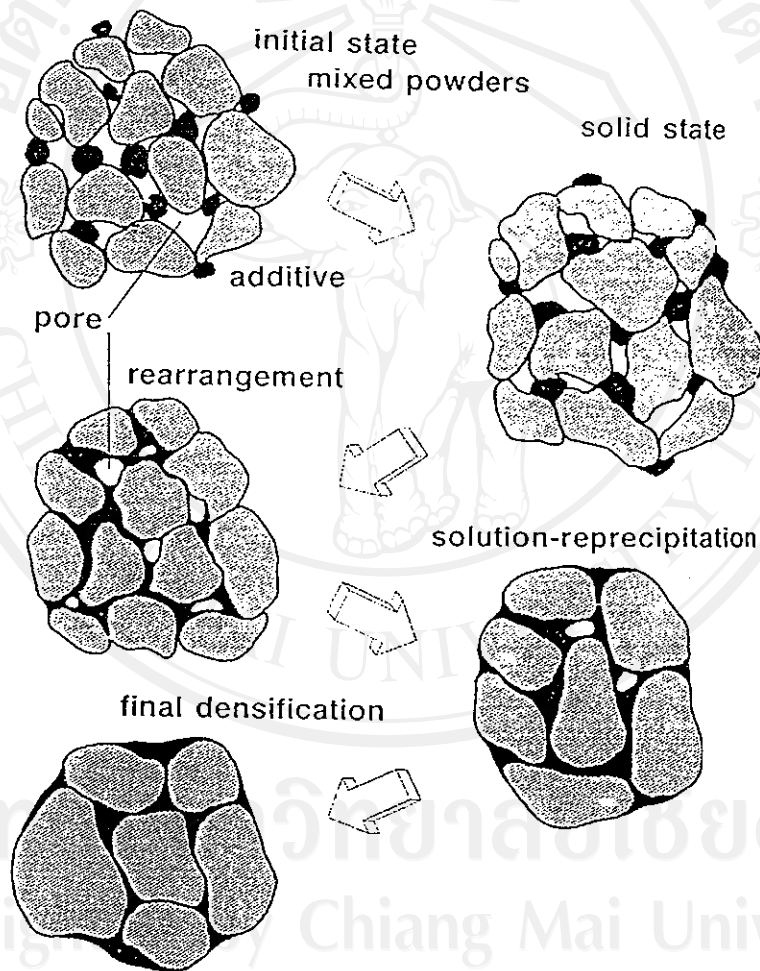


Figure 2.6 Schematic diagrams of the classic liquid-phase sintering stages involving mixed powders which form a non reactive liquid on heating, allowing subsequent particle rearrangement and densification by solution-precipitation and solid skeleton sintering [17].

The first step, particle rearrangement, involves formation and viscous flow of a liquid which wets the solid, initially forming liquid necks, spreads and draws the particles together by capillary pressure. The model suggests that liquid will tend to migrate to more densely packed regions first. Later when shrinkage has occurred, filling of the larger pores can result in the less densely packed regions becoming enriched with liquid. The second step, solution-precipitation, involves dissolving:

- i) Smaller solid particles in the liquid and precipitating on the solid surfaces of large particles. The small particles shrink and redeposit on larger ones because of their higher solubility in the liquid arising from their higher surface energy due to their small radius of curvature.
- ii) Particle-particle contacts (necks) and precipitation on uncompressed grain. The solubility of solid in liquid is increased by pressure at the contact points. This leads to material transport away from the necks and precipitation on large grains leading to grain growth.
- iii) Sharp corners (high convex shapes) and precipitating on lower convex or concave surfaces.

This is the critical step for densification and the presence of the capillary pressure allows additional particle rearrangement during grain growth. The third step, coalescence, is when enough grain growth has occurred to form a solid skeleton of particles so that the process of densification slows down and stop. In other words, the open pores become closed. The closed pores usually contain a gas from the sintering atmosphere.

The rate of liquid-phase sintering is also strongly affected by temperature. For most compositions a small increase in temperature result in a substantial increase

in the amount of liquid present. In some cases, this can be beneficial by increasing the rate of densification. In other cases, this can be detrimental by causing excessive grain growth or by allowing the part to slump and deform. Moreover, a range of microstructure can occur due to liquid-phase sintering. Major factors that lead to microstructure variations include the particle size, the amount of liquid present at the sintering temperature, and the cooling cycle.

2.3 Dielectric Behavior of BaTiO₃ Based Ceramics

Since 1940s, ferroelectric BaTiO₃ are frequently used to manufacture multilayer capacitors [8, 10, 18-21] owing to their high dielectric constant about 5,000-18,000 below its temperature (~ 130°C). Its crystal structure depends on the temperature. Below the T_c the structure is slightly distorted, with Ba²⁺ and Ti⁴⁺ ions displaced relatively to the O²⁻ ions, to the tetragonal form thereby creating a dipole moment along the *c* direction. A consideration of the ion displacements accompanying with the cubic-tetragonal transformation can give insight into how the spontaneous polarization might be coupled from unit cell to unit cell. X-ray studies have established that in the tetragonal form, taking the four central oxygen ions in the cubic phase as origin, the other ions are slightly shifted as shown in Figure 2.7. It is evident that if the central the Ti⁴⁺ ion is closer to one of the O²⁻ ions, it will be energetically favorable for the Ti⁴⁺ ion on the opposite side of O²⁻ ions be located at more distantly from that O²⁻ ion, thus engendering a similar displacement of all the Ti⁴⁺ ions in a particular column in the same direction. Coupling between neighboring columns occurs in BaTiO₃ so that all the Ti⁴⁺ ions are displaced in the same direction.

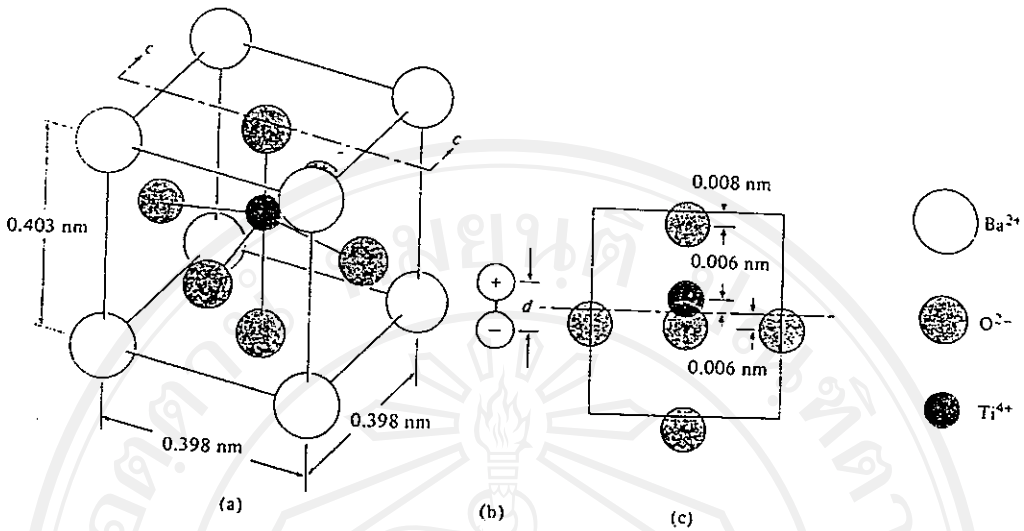


Figure 2.7 Approximate ion displacements in the cubic-tetragonal distortion in BaTiO₃: (a) Cubic; (b) Shift of centers of positive and negative charges; (c) Projection of tetragonal structure.

There is a vast literature on the properties of BaTiO₃ and the effects of various dopants on microstructure and on the properties. The idea of incorporating ions to this material in order to adjust or change its properties which makes them suitable for high performance capacitor dielectric in a wide temperature range. It is interesting to note that complex/mixed perovskite compound formed by substituting suitable single or multi ions at Ti-sites have yielded many interesting results.

2.4 Literature Surveys

2.4.1 Dielectric Properties of BaTiO₃ Based Ceramics

Many researchers, Tang, Weber and Armstrong [1-5] have been studied on the solid solution of other isovalent ions with partial substitution of Ti⁴⁺ like in Ba(Ti,Zr)O₃ and Ba(Ti,Sn)O₃ etc., to get smeared out in dielectric constant around the

Curie temperature (T_c) was found to exhibit diffuse phase transition (DPT), a similar behavior to well known complex ferroelectric relaxor. Diffuse phase transition which due to different ability of ions diffusion had effect to specimen homogeneity. This effect promoted to obtain more inhomogeneous region with different Curie point which show the flattened characteristic [8].

The influence of heterovalent substitution as acceptor, Mg^{2+} on their properties has been reported by many worker. Tkach *et al.* [14] reported that Mg ions may preferentially occupy at the B-site more than that A-site of $SrTiO_3$ perovskite lattice. Due to the ionic radius of Mg^{2+} is substantially smaller than 15 percent difference between the ionic size of Mg^{2+} and Sr^{2+} cations, have been indicated as the restricting factors for the solid solubility of Mg^{2+} at A and B-site is less than 2 mol percent [14, 22]. Above this concentration, second phase, $MgTiO_3$ and MgO , TiO_2 or $Ba_6Ti_{17}O_{40}$ were detected for A and B-substituted, respectively which indicating solubility limit in solid solution of Mg ion [22]. The effect of Mg ion on crystal structure was reported that an increase of lattice parameter, a , with Mg concentration. Base on size considerations the substitution of Ti^{4+} by bigger Mg^{2+} ions can lead to an expansion of cubic lattice [15]. This can be attributed to decrease the tetragonality, c/a , with increasing Mg concentration [14, 22-23]. In additional, the literature reported the Ti-site substitution by Mg^{2+} ions was exhibited p-type conduction. The oxygen vacancy was created to compensate charge balance in the system which gives rise to poor resistance [24-27]. The dielectric loss warped upwards markedly above 100 °C which is caused by the influence of leakage conductivity. Nagai *et al.* [22] observed that the dielectric constant, ϵ_r , tend to decrease with increasing Mg concentration and dielectric peak exhibited abnormally broadened which are different

from normal ferroelectric BT. Moreover, T_c shift to lower temperature ($\Delta T_c = -42\text{ }^\circ\text{C}$ where $x = 0-2$ mol percent), while the peak at tetragonal-orthorhombic transition temperature become broad without clear shift of temperature. Cause to inhomogeneous distribution of Mg^{2+} and Ti^{4+} would also lead to a DPT response, if the origin of the DPT was due to compositional fluctuations, as proposed by Smolenskii. The $\epsilon_r - T$ peak was markedly broadened due to the fine grain characteristic of the materials as well by controlling processing [28-30]. MgO as know as an unique dopant for alumina, as it enhances the densification rate and yet reduces the grain growth rate of alumina [31-32]. It is now widely agreed that the function of MgO is to prevent pore boundary separation and to inhibit abnormal grain growth. This assumes that the grain growth is controlled by co-exist the small amount of MgO with BT. Nagai *et al.* [22] observed that the grain size decreased with increasing Mg content and MgO residual was found at $x = 2$ mole percent due to solubility limit of diffusion of Mg into BT. These results suggest that the samples where $x < 2$ mol percent of Mg consist of a single phase of BT-based solid solution.

With partial doped the donor, Nb^{5+} into Ti-site in BT material has been reported by many researchers [33-41]. Ionic radius of Nb^{5+} and Ti^{4+} ions are closely 0.69 Å and 0.75 Å, respectively. According to the above detail there is a reason that Nb^{5+} ion replaced at Ti-site in BT lattice. Ferreira *et al.* [33] reported that 2 atom percent of Nb^{5+} doping was the maximum solubility limit and a second phase in the form of smaller grains was clearly seen. This result is quite agreed with Brzowski *et al.* [34] who found the second phase with the appearance of elongated needles shape in specimen doped with Nb^{5+} ion concentrations higher than 0.05 mole percent. The composition of the secondary phase corresponds to a non-stoichiometric compound

between $\text{Ba}_6\text{Ti}_{14}\text{Nb}_2\text{O}_{39}$ (in samples with low concentration of Nb^{5+} ion) and $\text{Ba}_6\text{Ti}_{17}\text{O}_{40}$ (in samples with high concentration of Nb^{5+} ion). Moreover, a diminution in tetragonality parameters with increase in Nb^{5+} ion concentration was observed.

According to above detail, the incorporation of Nb^{5+} substituting in Ti-site in the BT lattice produces the Ti segregation out of the grain [34-36]. This phenomenon promotes the liquid phase sintering at eutectic point, 1332 °C, due to A/B ratio was slightly shifted from 1. The fine grain, $\sim 1 \mu\text{m}$, is observed with high Nb^{5+} concentration, ≥ 0.15 mole percent cause by second phase formation at grain boundary to inhibit grain growth. Rahaman *et al.* [35] reported that the donor cation Nb^{5+} , the boundary mobility initially increased which cation concentration but then decreased markedly above the doping threshold of 0.3-0.5 atom percent. It means that over 0.3 atom percent, the reducing of grain size was found in BT ceramics. The influence of Nb^{5+} substitution on dielectric properties has been reported by Wu *et al.* [36]. They found the low concentration, 0.5 mole percent of Nb^{5+} , the sample showed significant decreasing the resistivity at room temperature and it changes into an insulator again because of the formation of ionic defects which compensate for the extra charge from donors [37]. The same result was found by Zhou and his colleagues [38] who found the resistivity decreases rapidly with the addition of 1 mole percent Nb^{5+} cation in SBT ceramics. Influence of Nb^{5+} on dielectric properties has been reported by Kahn [39]. He found that ϵ_r and T_c decreased with increasing the concentration of Nb^{5+} cation along with fine grain which showed ϵ_r higher than that big grain at room temperature. Diffuse phase transition was found at high concentration of Nb_2O_5 [39-41] due to the fine grain characteristic lead to introduces internal stresses in ceramics.

In 1971, Bonsack [42] reported the dielectric properties of pure BT were very sensitive to small of niobium (0.08-0.15 atom percent). BT-based ceramics were semiconductors, had high $\tan\delta$ and were useless as dielectric ceramic capacitors. If in addition to this niobium content, quantities of acceptor as Mg, Ca, Fe and Li was present, the effect of Nb was counteracted and ceramics were obtained having low conductivity and low $\tan\delta$ which are useful as capacitors. The same result was obtained by Chu who found the mostly BT compositions contained with donor, Nb^{5+} and Ta^{5+} and acceptor, Mg^{2+} and Co^{2+} reached a high ϵ_r . Chazono *et al.* [43-44] reported high ϵ_r is obtained when materials in the system BT-Nb-Co are used as the X7R dielectric materials which they exhibited a fine-grained microstructure and a compositional heterogeneity inside the grains, i.e., the core-shell structure. They have reported that, X7R-type materials are obtained when donor-rich compositions are used. Moreover, the core-shell structure was collapsed to homogeneous microstructure with increasing amount of acceptor (Co_3O_4) and sintering temperature. Recently, Yoon *et al.* [45-47] reported that the diffusion of dopants is suppressed in donor rich case (Nb), maintaining the core-shell structure. For the acceptor-rich case (Mg), observed a significant grain growth and enhanced solid-state diffusion that lead to collapse of the core-shell structure. The donor-rich fine-grained sample showed a very stable ϵ_r of ~ 1700 with temperature. In contrast, the acceptor-rich coarse-grained sample exhibited a peaked value of ϵ_r ($\sim 22,000$) at T_c (-50°C). They contributed that stability of ϵ_r of donor-rich sample is due to the core-shell structure and small grain size. Double substitution of Ti-site by Magnesium ion (Mg^{2+}) as acceptor coexist Niobium ion (Nb^{5+}) as donor, the enlarge of dielectric constant around T_c for ceramic specimen was reported by Weill *et al.* [48-49] with used chemical route preparation.

In their preparation, the compositions containing mostly BT with 4 mole percent of BMN content showed the maximum dielectric constant. A little bit different result that obtained from our previous work [50], the 2 mole percent of BMN doped BT exhibited the highest dielectric constant was prepared by high temperature solid solution method.

According to the study on defect chemistry of BT, Ba/Ti ratio has an important influence on sites-occupancy for the dopant ions. And also influence on the behavior and microstructure evolution of BT ceramics, which in turn is related to changes in the dielectric properties. When A/B ration >1 , BaO excess, the dopant ions tend to be on the B-sites. Moreover, the BT ceramics with excess Ba have fine-grain matrixes with 15 μm grains and relatively high ϵ_r at room temperature [51-52]. The phase transition became diffuse was reported in this case. The fine grain occurred by excess Ba is related to the suppression of grain growth due to the formation of second phase, Ba_2TiO_4 . However, high sintering temperature, 1539 $^\circ\text{C}$ is needed in this system.

In the case of A/B <1 , the small amount of excess Ti promoted liquid phase sintering to reduce the sintering temperature down at eutectic point, 1332 $^\circ\text{C}$, which is associated with the presence of the abnormal grain growth. The slightly Ti-excess composition was reported to have higher density. The liquid phase solidified as a Ti-excess grain boundary phase was expected to be $\text{Ba}_6\text{Ti}_{17}\text{O}_{40}$ or $\text{Ba}_4\text{Ti}_{13}\text{O}_{30}$. Moreover, the BT ceramic with excess Ti have large grain, 50 μm which along to be sharp transition behavior of ϵ_r at T_c was similar to that of stoichiometric (A/B = 1) composition.

Unfortunately, BaTiO₃ has a sintering temperature of ~ 1300°C. In addition to the increase in fabrication cost. So, a lowering of the sintering temperature is urgently needed to render BT ceramics more useful. One method of decreasing the sintering temperature is to add sintering aids that have low melting points and make liquid phases below the sintering temperature. BT ceramics with sintering temperatures down to about 1000 °C have been reported in the literature. The low melting point as sintering aids Bi₂O₃, Li₂CO₃, Na₂CO₃, B₂O₃, CdO and PbO were used to promote densification by liquid phase sintering. All of sintering aids can reduce the sintering temperature down below 1000 °C but unfortunately, lower sintering temperature are often accompanied by a significant decrease in ϵ_r . This decrease results mainly from dilution of the high ϵ_r with low ϵ_r of sintering aids or glass powder, and/or because of formation of low melting phase.

2.4.2 Effect of Low Sintering Aids on Dielectric Properties of BaTiO₃ Based Ceramics

In 1982, Ian *et. al.* [68] proposed that dielectric properties of BT with sintering aids depend on radius of ions and its chemical properties such as valency and electronegativity of sintering aids. The reported that Lithium oxide is a benefit for liquid-phase sintering BT and was used mainly because of its relatively low vapor pressure to promote denser microstructure of ceramic than other monovalent oxides. The same result was found by Cheng *et. al.* [69,70] who found the slightly higher value in both linear shrinkage and densities for Li₂CO₃-added PZT ceramics than that of Na₂CO₃-added. Lower diffusion rate of Na⁺ compared with Li⁺ seems to be the cause of this result. Because of its small ionic radius (0.6Å), Li⁺ is mobile in the ceramic and can diffuse into grain which effect on charge imbalance in ceramic. This

result reflected by increase $\tan\delta$ when temperature is higher than T_c . Moreover, Li_2CO_3 added into the BT-based system, the ϵ_r of this system at high temperature near the T_c was improved. Also, the ϵ_r at low temperature will be depressed at the same time. This result was proposed by Li *et. al.* [71] In order to balance out the charge fluctuation caused by Li^+ and to suppress the possibility of defect formation, trivalent oxide (Bi_2O_3) is also added together with Li_2CO_3 . Many works have been reported the sintering behavior of BT coexist with Bi_2O_3 . Bi_2O_3 -doped BT widespread use as ceramic capacitor because of its significant effect on lowering the sintering temperatures whose low melting point is 825 ± 3 °C [72]. Zhou *et. al.* [73] reported that the solubility of Bi_2O_3 in BT is 3 at% which is detected by SEM and X-ray technique. When Bi exceeds the solubility limit, a second phase, $\text{Bi}_2\text{Ti}_2\text{O}_7$, with a long needle shape, is detected. Moreover, as the Bi content increase, although c monotonously decreases and a slightly increase. The decrease of the unit cell volume can be attributed to the smaller ionic radius of Bi^{3+} (0.96 Å) compared to that of Ba^{2+} (1.5 Å). Bi_2O_3 doping significantly decreases the grain size. This result can be confirmed by Kim *et. al.* [74] who found the diffusion of Bi ions into Ba-site reflected on the X-ray diffraction peaks were broadening. This phenomenon may be connected with decreasing on grain size with increasing of Bi content. They proposed the ϵ_r and $\tan\delta$ were decreased with increasing Bi content in the BST thin films. Moreover, Bi_2O_3 is also used as donor dopant for BT-base PCT thermistors.

According to Ian reported the electron-probe analysis of the ceramic grains of samples sintered with good compositional homogeneity indicated essentially complete absorption of Bi ion from the flux into the ceramic. Additionally, Bi_2O_3 concentration was 3 wt% for the optimum values of ϵ_r . At high Bi_2O_3 levels

(> 3wt%) the ϵ_r peak was depressed below room temperature and broadened. He suggested the possibility that the Bi_2O_3 could have substituted in the ceramic on Ti-site at Bi^{5+} . The site occupancy of Bi ion in similar ceramic dielectrics has also been discussed by Maher [75]. He proposed that approximately the 1 mole% of Bi_2O_3 tended to enter the lattice as Bi^{5+} , presumably on the Ti-site, and causes an upward shift in T_c . Above 1 mole%, the Bi_2O_3 tended to enter the lattice as Bi^{3+} , presumably on the Ba-site, and causes a downward shift in T_c . Moreover, Bi_2O_3 used for enhance sintering without grain growth, in order to achieve an X7R type characteristic.

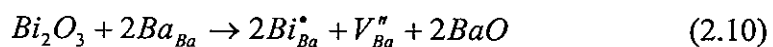
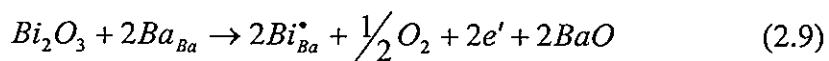
Binary and ternary sintering aids systems to modify BT with, B_2O_3 , Bi_2O_3 and CdO. It was found that ceramics sintered at 1100 °C would permit grain growth during sintering and produce dielectric constant greater than 5,000 at room temperature. Halder *et al.* [76] reported that BT based ceramics containing lithium tetraborate and bismuth oxide (sintering aids and Curie peak suppressor) can be fired in an inert atmosphere (argon). This composition can increase the dielectric constant and loss tangent but can be suppressed by adding a small amount of MnO_2 in the matrix. The interstitial effect with Li^+ exhibited an anomalous increase of $\tan\delta$ when temperature is higher than T_c . Moreover, ϵ_r is decreased with increasing concentration of Lithium oxide because the ϵ_r of sintering aids are lower than those of the ceramics. Later, Cheng [69-70], used the suitable additives such as Li_2CO_3 , Bi_2O_3 , B_2O_3 , Na_2CO_3 and V_2O_3 , to reduce the sintering temperature of PZT ceramics as low as 1070 °C. By using monovalent together with trivalent oxides as liquid phase former such as $\text{Li}_2\text{CO}_3/\text{Bi}_2\text{O}_3$ and $\text{Li}_2\text{CO}_3/\text{V}_2\text{O}_3$ which are added in the same mole fraction due to charge compensation. The optimum condition was at 0.375 wt percent of $\text{Bi}_2\text{O}_3/\text{Li}_2\text{CO}_3$ which showed good piezoelectric properties. After that, he

has been reported [77] that $(100-x)$ PMN_{0.85}PT_{0.15} - x Bi₂O₃/Li₂O, where the sintering temperature is 900 °C with $x > 2$. The ϵ_r of PMN_{0.85}PT_{0.15} - x Bi₂O₃/Li₂O was decrease with increasing x . The ϵ_r -T curve indicated that DPT is enhanced with the incorporation of Bi₂O₃/Li₂O. For $x = 4$, showed the ϵ_r was about 8000 at 40 °C. For $x = 8$, Bi₂O₃/Li₂O phases were detected as second phase at grain boundary, indicating that excess sintering aids, Bi₂O₃/Li₂O may segregated along the grain boundary. Zhou *et. al.* [78] proposed that the resultant formation was BST-Nb with 2 mole% 3Li₂O.2SiO₂+0.2 mole%Bi₂O₃, the sintering temperature can be decreased to 1100 °C and the sample changes from semiconductor to insulator due to Bi can diffuse to the grain boundary to form an insulating layer. The dielectric properties of resultant ceramics are $\epsilon_r = 25,000$, $\tan\delta = 2 \%$ and $\rho = 10^{10}\Omega.cm$ which was suitable for the capacitor application.

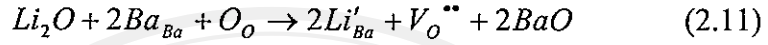
In case BT, mostly Li⁺ ions and Bi³⁺ ions undergo Ba-site substitution. The diffusion of impurities into the grain exhibited the shift of T_c toward a lower temperature and dielectric constant decreases compared with that of un-sintering aids. Additionally, c/a ratio was decreased with increasing amount of Li₂CO₃/Bi₂O₃ cause by lattice distortion due to substituted by smaller ionic radius than Ba²⁺ ions.

In charge balance compensation mechanism when Ba²⁺ is replaced by Bi³⁺ as donor and Li⁺ as acceptor are following defect reaction equation.

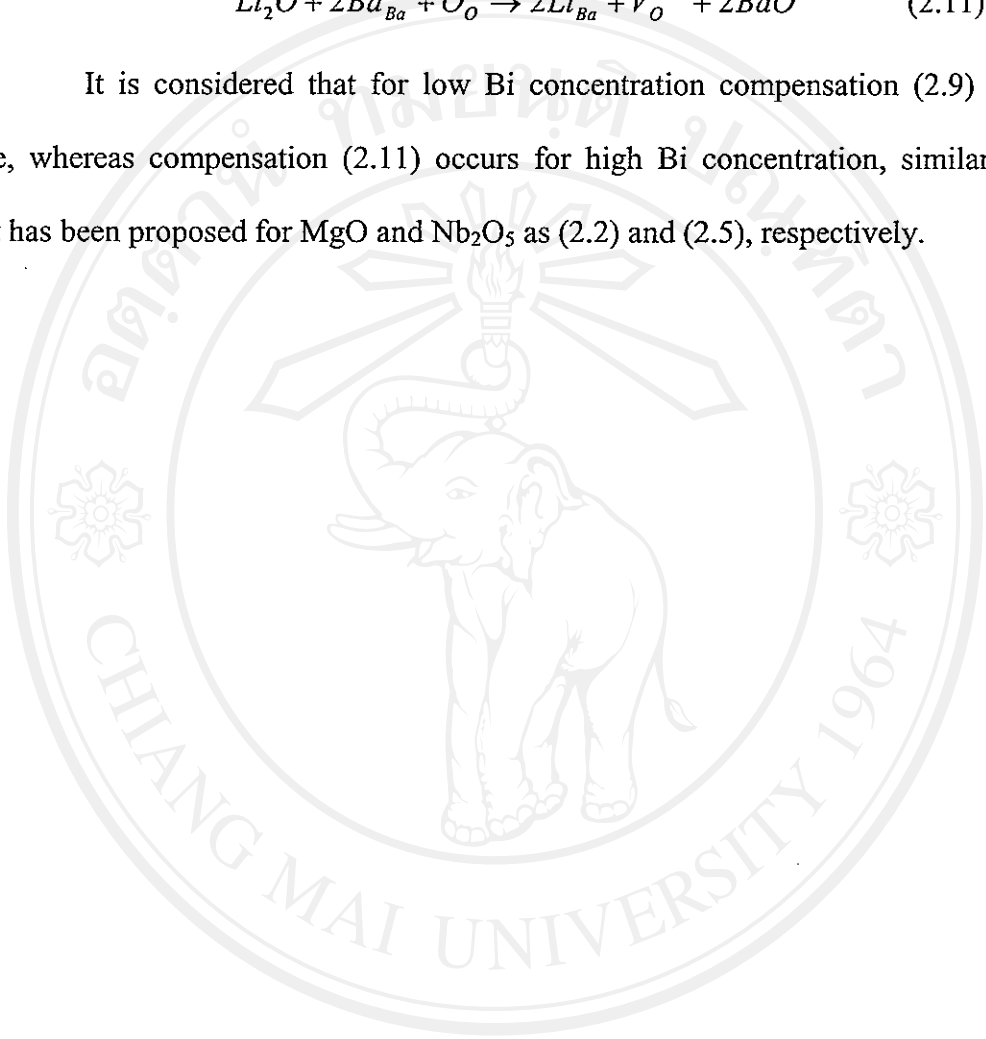
For Bi³⁺ ions,



For Li^+ ions,



It is considered that for low Bi concentration compensation (2.9) takes place, whereas compensation (2.11) occurs for high Bi concentration, similarly to what has been proposed for MgO and Nb_2O_5 as (2.2) and (2.5), respectively.



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