CHAPTER - 2

PREPARATION OF FERROELECTRIC CERAMICS

2. 1 Introduction

The subject of ceramics covers a wide range of materials. Recent attempts have been made to divide it into two parts "traditional ceramics" and "advanced ceramics". The use of the term “advanced” has however, not received general acceptance, and other terms, including “technical”, “special”, “fine”, and “engineering” are also encountered. Advanced ceramics include ceramics for electrical, magnetic, electronic and optical applications (sometimes referred to as functional ceramics) and ceramics for structural applications at ambient as well as elevated temperatures (structural ceramics).

Chemically, with the exception of carbon, ceramics are non metallic, inorganic compounds. Usually, ceramics are oxides or non-oxides composed of metallic and non-metallic elements (including carbon). The term ‘ceramics’ comes from keramos, the ancient greek word for objects made of fired clay.

2. 2 Preparation of advanced ceramics

Although a broad overlap exists between traditional ceramics and advanced ceramics with regard to raw material source, raw materials for advanced ceramics are usually chemically prepared materials of high purity. The powder process routes vary greatly, but several common objectives for all processes are high chemical purity, controlled particle size and distribution, high reactivity, and freedom from hard agglomerates or aggregates that will not break down during mixing and subsequent processing.

The optimum particle size distribution for ceramic powders is still a controversial issue. Fine, mono-sized spherical particles of about 100 nm diameter are best for ordered packing in to dense bodies and are highly reactive. Furthermore, these particles are of uniform size and they sinter well with little tendency toward exaggerated grain growth.
Unfortunately, even the best packing of mono-sized spheres, in practice, leaves a 30% interstitial void volume. Hence a great amount of sintering and shrinkage is required to achieve full density. Alternatively an extended distribution of particle sizes from approximately 20 μm to less than 50 nm allows highly efficient packing with an interstitial pore volume of less than 5%. Thus much less sintering is required to achieve full density. Unfortunately the larger particles often grow excessively during sintering, resulting in microstructures that are not ideal. Some intermediate position between these two particle sizes approaches is likely to produce the best results.

The commonly used methods for the consolidation of ceramic powders are described here. The microstructure of the consolidated powder form has a significant effect during sintering stages. The uniform packing of particles in the green body is the goal of the consolidation step. Since the packing density controls the amount of shrinkage during firing, the achievement of high packing densities is also desirable. Mechanical compaction of dry or semidry powder in a die is mainly done in ceramic preparation. In general, the applied pressure is not transmitted uniformly because of friction between the particles themselves and between the particles and the walls of the die. The stress variations lead to density variations in the compacted powder, thereby placing considerable limits on the degree of packing uniformity that can be achieved.

2.2.1 Weighing and mixing

The first step in the preparation of a ceramic is to weigh out the raw material with due allowance for impurity and moisture content. The carbonates and oxides of the constituent salts were weighed stoichiometrically and mixed in an agate mortar. It is then crushed and mixed in presence of excess methanol and is calcined. The calcined power is again crushed and ground finely again. Appropriate quantities of polyvinyl alcohol (binder) is added and is mixed with the powder.

2.2.2 Dry and semidry pressing methods

Dry pressing and isostatic pressing are commonly used for the compaction of dry powder which typically contain < 2% water and semidry powders, which contain 5-20 wt %
water. Die compaction is one of the most widely used operations in ceramic processing. However, the agglomeration of dry powders combined with non-uniform transmission of the applied pressure during compaction leads to significant variations in the packing density of the green body. To minimize density variations, die pressing is used for the production of relatively simple shapes (e.g. disks) with a length to diameter ratio 0.5 - 1. Isostatic pressing produces better uniformity in the packing density and can be used for production of green bodies with relatively complex shapes and with much higher length to diameter ratios. For the preparation of ferroelectric ceramic pellets, we have designed and fabricated a die (mould) using die steel. The schematic diagram of the die is shown in figure 2.1 (A). This die can be used to apply a pressure up to 7000 Kg /Inch². Using this die cylindrical pellets of 10 mm diameter and thickness 10-20 mm can be easily made, by filling it with the powder and pressing under a hydraulic press with appropriate pressure.

2.2.3 Die compaction

Die compaction involves simultaneous uni-axial compaction and shaping of a powder or granular material in a rigid die. It allows the formation of relatively simple shapes rapidly with accurate dimensions. The overall process consists of filling the die, compacting the powder, and ejecting the compacted powder. After the completion of the die compaction process, we require that the green body be free of defects and that gradients in the packing density be as low as possible. Density gradients in the green body can lead to heterogeneities in the fired body that causes a degradation in properties. A number of factors can be controlled to reduce the extent of density gradients in the powder compact. Good filling of the die with the powder reduces the amount of internal movement of the powder during the compaction process. The use of lubricants to reduce the internal friction between the particles and the die wall can lead to significant improvements.

Two of the most common defects in die compact powders are delamination and end capping shown in figure 2.1 (B) and (C). These defects are caused by differential strain recovery during the ejection of the compact form from the die. The use of small amounts of binder to increase the compact strength, reduction of the applied pressure to reduce the extent of the spring back and the use of lubricant to reduce die wall friction can significantly reduce the tendency for elimination and end caps to form.
Figure 2.1 showing the schematic diagram of (A) die (mould) made of die steel used for making the ferroelectric ceramic pellets. (B) delamination (C) end capping.

2.3 Sintering and densification processes in practice

In simplest situations, there are two heating schedule commonly used in sintering experiments. In many cases the powder compact is heated rapidly to a fixed sintering temperature, held at this temperature for the required time, and finally cooled to room temperature. This schedule is referred to as isothermal sintering. In the other case referred to as constant heating rate sintering, the compact is heated at a fixed rate to the required temperature, after which it is cooled. For powder systems in which the coarsening rate is higher than the densification rate at lower temperature isothermal sintering may have an advantage from the point of view of achieving high density; the powder compact spends less time at lower temperature where coarsening dominates over densification.

2.3.1 Sintering process variables

Two of the most important variables in conventional sintering are the firing schedule and the atmosphere surrounding the sample. These two variables, in particular the firing schedule, have received considerably less attention than other process variables (e.g., particle size). In many cases an arbitrary schedule is used in some convenient atmosphere. However, the effect of these two variables are fairly well understood, and their control can provide an effective and important approach for altering the microstructure of the fabricated article in the desired direction.
Kinetic data for the densification of the powder compact during sintering are important practically and theoretically. They can be obtained as functions of time or temperature by the following two methods: (i) intermittently, by measuring the density of a powder compact fired to a given temperature or for a given period of time, or (ii) continuously by the technique of dilatometry. The intermittent method is time consuming. A different sample is used for each run, and the density of the fired sample is determined from its mass and dimensions (for a regular geometry), by Archimede's method, or by both these methods.

2.3.2 Control of the heating schedule

For single-phase powders that do not undergo a phase transformation and have been consolidated without a binder, the heating schedule can be relatively simple. The powder compact is heated rapidly or at a controlled rate to an isothermal sintering temperature, held at this temperature for the required time to accomplish the desired density, and finally cooled. The preheating and sintering were done using high temperature furnace in our laboratory. Figure 2.2 show the photograph of high temperature furnace, which uses a microprocessor based PID temperature control unit. The heating elements used are silicon carbide rods. The furnace can be programmed for any heating schedules. In general, the heating schedule for more complex systems can consist of several stages. A multistage system is described in the following way.

Stage 1: Binder burnout

Stage 1 may consist of a binder burnout stage during which the sample is heated slowly (typically <5º/min) and held at a temperature in the range of 400-500º C for the required time. The time required for the binder burnout depended on the size of the sample and the amount of binder. It can vary from 1 hour for small pellets used in research to several days for large injection-molded parts. During this stage, an oxidizing atmosphere is beneficial for complete removal of the binder. Carbonaceous residues can react with the powder to form unwanted phases (e.g., oxy-carbides in some oxide ceramics) and microstructural flaws in the fabricated article.
Figure 2. 2 show the photograph of high temperature furnace using silicon carbide heating elements, on the right side the control unit, which uses a microprocessor based PID temperature control system.

If the powder compact contains phases that can undergo significant oxidation at the binder burnout temperature, removal of the binder must be accomplished in an inert atmosphere (e.g., Argon). In this case, a binder with good burnout characteristics in a non oxidizing atmosphere should be selected at the outset of processing.

Stage 2: Low temperature soak.
The second stage of the heating schedule may involve a low-temperature soak. The powder compact is heated to a temperature below that of the onset of densification but sufficiently high to cause chemical homogenization or to modify the microstructure. Chemical homogenization may involve a solid-state reaction in which a small amount of dopant is incorporated into the powder or a reaction leading to the formation of a liquid phase. The precoarsening of a heterogeneous powder compact, for example, provides the microstructural modification that can be accomplished during this stage. However, this type of microstructural modification is rarely performed.
Stage 3: Heat-up to the sintering temperature

The heat-up stage involves heating the powder compact to the isothermal sintering temperature. The rate of sintering should be carefully controlled to develop the required microstructure in the final article. It is often observed that a faster heating rate at this stage enhances the densification in the subsequent isothermal sintering stage. A possible explanation of this observation is that the coarsening of the powder during heat-up is reduced due to the shorter time taken to reach the isothermal sintering temperature. Thus, the powder compact has a finer microstructure at the start of isothermal sintering. Fast heating rates can be achieved by pushing the powder compact at a controlled rate into a furnace preheated to the desired temperature. However, for large articles it is important to limit rapid temperature changes so as to avoid large temperature gradients between the surface and the interior of the article. Large gradients can lead to cracking. They can also lead to premature densification of a surface layer that hinders the densification of the interior of the compact.

Stage 4: Isothermal sintering

The isothermal sintering temperature is chosen to be as low as possible yet compatible with the requirement that densification be achieved within a reasonable time (typically less than 5 hours). Longer sintering time may be needed if the sintering process involves a chemical homogenization between reactant powders. Higher sintering temperatures lead to faster densification, but the rate of coarsening also increases. The increased coarsening rate may lead to abnormal grain growth with pores trapped inside large grains. Thus, although densification proceeds faster, the final density may be limited.

Stage 5: Cooling

After densification, the article is cooled to room temperature or, in some cases to an annealing temperature at which thermal stresses are reduced or some modification of the chemical composition or of the microstructure is carried out. The cooling rate can be fairly fast for relatively small articles. However, for large articles the cooling rate is much slower to prevent large temperature gradients that can lead to cracking. When
compositional or microstructural modification must be achieved, the cooling rate needs to be carefully controlled. The cooling rate can influence the precipitation of second phases and their distribution in the fabricated article. Figure 2.3 shows the schematic representation which gives better representation of the different stages of the heating schedule.

![](image)

**Figure 2.3 Sketch of general heating schedule**

2.3.3 Solid-state Reactions

Chemical decomposition reaction, in which a solid reactant is heated to produce a new solid plus a gas, are commonly used for the production of powder of simple oxides from carbonates, hydroxides, nitrates, sulphates, acetates, oxalates, alkoxides, and other metal salts. The decomposition of SrCO$_3$, BaCO$_3$ and Nb$_2$O$_5$ to produce Sr$_{1-x}$Ba$_x$Nb$_2$O$_6$ and carbon dioxide gas as below.

\[
(1-x) \text{SrCO}_3 + \text{BaCO}_3 + \text{Nb}_2\text{O}_5 \Rightarrow \text{Sr}_{1-x}\text{Ba}_x\text{Nb}_2\text{O}_6 + \text{CO}_2 (g) \quad (2.1)
\]

Chemical reaction between solid starting materials, usually in the form of mixed powders, are common for the production of powders of complex oxides such as Niobates, titanates, ferrites, and silicates. The reactants normally consists of simple oxides, carbonates: An example is the reaction between barium carbonate, and sodium carbonate and niobium pentoxide.
4 \( \text{BaCO}_3 + \text{Na}_2\text{CO}_3 + 5 \text{Nb}_2\text{O}_5 \rightarrow \text{Ba}_4\text{Na}_2\text{Nb}_{10}\text{O}_{30} + 5 \text{CO}_2 \text{(g)} \) (2.2)

These reactions, involving decomposition of solids or chemical reaction between solids, are referred to in the ceramic literature as calcination.

### 2.4 Calcination

Calcination processes are endothermic decomposition reactions in which an oxysalt, such as carbonate or hydroxide, decomposes, leaving an oxide as a solid product liberating a gas. Calcination is often the final step in the production of high-purity ceramic powders. Soluble salts are commonly used as the ceramic precursor to make an easily purified solution. After purification, a calcinable salt is precipitated from solution by adding hydroxide, carbonate, or similar materials. The salt is then calcined to yield the pure oxide.

Calcination reaction often plays a major role in the synthesis of multi-component ceramic compounds. If compound formation is to occur during calcining or firing, the matter of neighbouring particles must inter diffuse and the time taken to complete the process is proportional to the square of the particle size. The process will clearly be considerably slower if the particles consist of aggregates of crystals rather than individual crystals.

### 2.5 Porous Materials

In the majority of electrical applications sintered ceramics are required to have minimum porosity. Properties usually reach their optimum values at the highest densities. Whilst porosity in excess of 5% - 10% allows the ingress of moisture, leading to many serious problems. However, there are cases where porosity is desirable. For example, in humidity and gas sensors and where thermal shock resistance is of overriding importance. Porous structures can be obtained in the following ways.

1. Calcining at a high temperature so that considerable crystal growth takes place and, after grinding coarsely, separating out particles in a limited size range. Bodies compacted and sintered from such powders will have continuous porosity.
and cavities as large as 30μm. The total accessible specific surface area will be low.

2. Underfiring an otherwise normally processed body. The pore structures will be fine and the total accessible specific surface area is high.

3. Mixing organic or carbon particles with diameters exceeding 20μm into a ceramic powder, cavities of corresponding size are left after burning out and sintering. The content of such particles need to exceed 20 vol. % if porosity is to be continuous. The method allows a control over the final structure that is largely independent of the sintering conditions.

4. High porosity is obtained by using a high proportion of binder containing a foaming agent. Gas is generated within a liquid binder-powder mixture that subsequently becomes rigid through the polymerization of the binder. The porosity may be either continuous or discontinuous according to the formation of the binder and is little changed by burn-out and sintering. Materials containing large cavities (several millimeters) can be formed in this way.

5. An existing porous structure, e.g., certain coral, can be reproduced by impregnating it with wax and then dissolving out the original solid (calcium carbonate in the case of coral). The porous wax structure is then impregnated with a concentrated slip containing the ceramic powder. After drying, the wax can be melted out and the ceramic fired. The method becomes more economic if a suitable foam with a continuous porosity is impregnated with a slip and then burned out. In this case the final ceramic structure corresponds to the vacant spaces with in the foam.

2.6 Binder Systems
Although the binder plays a transient role in the overall fabrication route, careful selection of a binder is vital to the success of ceramic fabrication process. The binder must provide the desired rheological properties to the feed material so that the powder can be consolidated into the desired shape and then can be removed completely from the shaped powder form, prior to firing, without the disruption of the particle packing or any chemical reaction with the powder. A good binder must therefore have desirable
rheological characteristics, chemical characteristics, and binder burnout behaviour. A single binder cannot satisfy all these requirements, so in practice a combination of several additives is used. It turns out that the use of a binder system consisting of several additives may be beneficial for the binder burnout step in that the additives can be removed progressively as dictated by their volatility or chemical reactivity. The removal of first binder creates a network of porosity through which the decomposition products of the second binder can be removed more easily.

Binder systems for ceramic materials have generally been developed on a trial and error basis. However, a number of key issues arise in their formulation. One of these is the type of binder system, because it is used in most injection moulding operations. The binder system generally consists of three components: a major binder, a minor binder, and small amounts of additives used as processing aids. The major binder controls the rheology of the feed material during die pressing to produce a body free of defects and also controls the strength of the green body and the binder burnout behaviour. The minor binder is used to modify the flow properties of the feed material for good filling of the mould. The processing aids may include one or all of the following: a surfactant to improve the wetting between the particle surfaces and the polymer melt, a lubricant to reduce inter-particle and die-wall friction and a plasticizer to control the viscosity of the feed material. Table 2.1 below lists some commonly used additives employed in the formulation of thermoplastic binder systems in the injection moulding of ceramics [1].

Table 2.1 Substances commonly employed in the formulation of thermoplastic binder systems for the ceramic fabrication process.

<table>
<thead>
<tr>
<th>Major binder</th>
<th>Minor binder</th>
<th>Plasticizer</th>
<th>Other additive</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polypropylene</td>
<td>Microcrystalline</td>
<td>Dimethyl phthalate</td>
<td>Steric acid</td>
</tr>
<tr>
<td>Polyethylene</td>
<td>Wax</td>
<td>Diethyl phthalate</td>
<td>Oleic acid</td>
</tr>
<tr>
<td>Polystyrene</td>
<td>Paraffin wax</td>
<td>Dibutyl phthalate</td>
<td>Fish oil</td>
</tr>
<tr>
<td>Poly (vinyl acetate)</td>
<td>Vegetable oil</td>
<td>Dioctyl phthalate</td>
<td>Organosilane</td>
</tr>
<tr>
<td>Poly (methylmethacrylate)</td>
<td>Carnauba wax</td>
<td></td>
<td>Organotitanate</td>
</tr>
</tbody>
</table>

Another important issue is the amount of binder in the feed material. Assuming that in die-moulding operation the particles achieve a packing arrangement close to that
of dense random packing, then the amount of binder required to fill the interstices between the particles is roughly 35-40%. However, other factors must be taken into account. While a high packing density of the particles is desirable, the mixture must also have a low enough viscosity for mold filling. Too little binder leads to a high viscosity and defects in the moulded body, where as excess binder leads to distortion of the moulded body, and disruption of the particle packing arrangement in the binder burnout step. Rheological characterization of binder systems and of powder- binder mixtures has an important role to play in striking the best balance between formability and binder content. In practice, depending on the characteristics of the powder and binder, the amount of binder ranges form 15 to 50 vol%.

2.6.1 Mixing of the feed material
Homogeneous mixing of the powder and binder is essential. Mixing is usually performed by adding the powder to the molten binder in a shear mixer. Initially a high torque develops as the powder is added to the binder due to high friction between the mixer and the powder agglomerates that have not yet been coated with the binder. As mixing continues, the torque decreases gradually as more powder is wetted by the binder and more powder agglomerates are broken down. Contamination by aberration is a common problem during the initial period of high torque. Although a high shear rate is normally used in the final stages of mixing, insufficient breakdown of the agglomerate and therefore inhomogeneous mixing are serious problems. After cooling, the mixer is filled in the die, where it is converted into cylindrical discs with a diameter of 10 mm.

2.6.2 Binder removal
The binder must be removed from the green body prior to firing at an elevated temperature to produce the final ceramic pellets. Ideally, we would like to remove the binder completely without disrupting the packing of the particles or producing any new defects in the green body. Residual contaminants such as carbon and inorganic ions and defects such as cracks and large voids affect the microstructural evolution during firing and hence the properties of the ceramic samples. Binder removal is a critical step in ceramic processing, especially in the case of forming methods such as tape casting and
injection moulding where the binder content in the green body is relatively high. The process of binder removal is also referred to as debinding. Binder removal can be accomplished thermally by heating the green body at slightly elevated temperatures or by dissolution of the binder in a solvent. While the solvent extraction approach finds some use in practice, it suffers from a number of limitations. Here, we shall consider the thermal debinding process commonly referred to as binder burnout.

Thermal debinding of ceramics is a complex process that is influenced by both chemical and physical factors. Chemically, the composition of the binder determines the decomposition temperature and the decomposition products. Physically, the removal of the binder is controlled by heat transfer into the body and mass transport of the decomposition products out of the body. In practice, complications arising from the use of binder systems consisting of three or four additives that differ in volatility and chemical decomposition must also be taken into account. Furthermore, the ceramic powder may alter the decomposition of the pure polymer. In view of its complexity, a more detailed discussion of the thermal debinding process cannot be provided in the limited space remaining in this chapter.

2.6.3 Stage and mechanisms of thermal debinding
The process of thermal debinding of a thermoplastic binder can be roughly divided into the following three stages.

Stage I involves heating the binder initially to a point where it softens e.g., \( \approx 150-200°C \). Chemical decomposition and binder removal are negligible in this stage, but a number of processes occur that can have serious consequences on the control of the shape and structural uniformity of the body. These processes include shrinkage, deformation and bubble formation. Shrinkage occurs by a rearrangement process as the particles try to achieve denser packing under the action of the surface tension of the polymer melt. Deformation is promoted by a lower packing density in the green body, higher binder content and lower melt viscosity. Bubble formation results from the decomposition of the binder as well as from residual solvent, dissolved air, or air bubbles trapped within the green body during forming. The formation of bubbles is a possible source of failure or
defect formation during thermal debinding.

In stage 2, typically covering a temperature range of 200-400°C, most of the binder is removed by evaporation and chemical decomposition. Appreciable capillary flow of the molten polymer can accompany the evaporation process. The nature of the decomposition reactions depends on the chemical composition of the polymer and on the atmosphere. In inert atmospheres such as nitrogen or argon, polymers such as polyethylene undergo thermal degradation by chain scission at random points in the main chain to form smaller chain segments. The formation of smaller chain segments leads to a reduction in the polymer viscosity. With continued thermal degradation, the chain segments become small enough (i.e., their volatility increases) that evaporation is promoted. Other polymers (e.g., poly vinyl methacrylate) undergo depolymerisation reactions to produce a high percentage of volatile monomers. In oxidizing atmospheres, degradation by oxidation occurs in addition to thermal degradation. Oxidative degradation commonly occurs by a free radical mechanism to produce decomposition products that contain a high percentage of volatile, low molecular weight compounds such as water, carbon dioxide, and carbon monoxide. Compared to thermal degradation, oxidation reactions generally lead to decomposition at lower temperatures and to an increase in the rate at which the binder is removed.

Finally, in stage 3, the small amount of binders still remaining in the body is removed by evaporation and decomposition at temperatures above \( \approx 400°C \). The highly porous nature of the body facilitates the removal of the binder. However, the atmosphere must be carefully chosen to avoid the retention of an excessive amount of binder residue.

2.6.4 Models for thermal debinding

Practical binder systems normally contain low molecular weight, volatile components that can undergo evaporation without thermal degradation. In general, three models need to be considered: (i) thermal degradation, (ii) oxidative degradation, and (iii) evaporation.

Thermal degradation leads to the production of volatile, low molecular weight products through out the binder phase. The rate of evaporation at the surface and the rate of transport of the degradation products through the body determine the concentration
profile of the products. Volatile products present in the centre of the body must not be allowed to reach temperatures above their boiling point because this would lead to the formation of bubbles and hence, defects. Thermal degradation therefore involves removal of the binder by evaporation of a liquid.

Binder removal during thermal degradation may be quite similar to the drying of moist granular material. Let us consider a model in which interconnected pores of two different radii are present. Even though the pores have different radii \( r_1 \) and \( r_2 \), initially liquid evaporates from them at the same rate so that the radii of the menisci \( r_m \) are equal. The capillary tension in the liquid is given by the equation 2.3 [1].

\[
P = 2 \gamma_{lv} / \gamma_m \chi
\]

where \( \gamma_{lv} \) is the surface tension of the liquid. If the radii of the menisci were different, the capillary tension given by the above equation would also be different and liquid would flow from one pore to the other until the menisci become equal again. As evaporation from the surface proceeds, the radii of the menisci decreases. However, almost no shrinkage of the body occurs because the particles are practically touching. A point is reached where the radii of the menisci is equal to the radius of the larger pore, i.e., \( \gamma_m = \gamma_l \). Further evaporation forces the liquid to retreat into the large pore. However, the radius of the meniscus, \( r_m \), will continue to decrease in the small pore and the capillary tension will suck liquid from the large pore. In this way the large pore implies first and the small pore remains full of liquid. After the large pore has been emptied, the small pore starts to empty.

In practice we will have a distribution of pore sizes and pore shapes. However, the same principles discussed above will apply. The largest pores empty first and the smallest empty last. Pore channels first develop deep in the body as liquid from the larger pores is drawn into the smaller pores. We see that considerable redistribution of the liquid would be expected to occur during thermal degradation.

In the evaporation model, the volatile components are distributed throughout the
binder phase. However, this model differs from the thermal degradation model only in that the volatile components are already present in the binder at some initial concentration. As the volatile components diffuse to the surface and evaporates, their concentration decreases. In thermal degradation, the volatile products have a concentration that is initially zero, but increases with degradation and then decreases as the volatile products diffuse to the surface and evaporate. The model discussed earlier for the thermal degradation case is also expected to describe the main features of the evaporation of volatile, low molecular weight components that do not undergo thermal degradation. Recent observations do indicate that the removal of such components in binder system leads to the development of porosity and liquid redistribution along the lines outlined for the thermal degradation model.

In oxidative degradation, the reaction occurs at the polymer/gas interface, which recedes into the body as degradation proceeds. The reaction products are gaseous and must be removed by diffusion or permeation through the porous outer layer. This model is analogous to the shrinking core model for the production of powders by calcination. The mean free path of the gaseous reaction products determine whether diffusion or permeation controls the transport of the gases through the porous outer layer. For the model shown in figure 2.4, assuming that the binder is removed isothermally as a single component, low molecular weight vapour, the time for removal of the binder depends on several parameters [2]. Small particle size and

Figure 2.4 Schematic diagram of the model for thermal debinding by oxidative
degradation where the binder/vapour interface is at a distance $L$ from the surface of the compact.

low porosity reduce the rate of binder removal. However, small particle size and low porosity enhance densification during the firing process. A conflict therefore exists between rapid removal of the binder and the achievement of high densification. One solution to the conflict might involve the use of sintering aid that enhances the densification process during firing. A low ambient pressure or vacuum serves to reduce the time for binder removal. A vacuum, however, does not lead to oxidative degradation. Furthermore, temperature control and transport of heat are poor in vacuum. The use of an oxidizing gas at reduced ambient pressure may provide adequate degradation as well as good thermal transport.

2.7 Sintering mechanisms

Polycrystalline materials sinter by diffusional transport of matter whereas amorphous materials sinter by viscous flow. In polycrystalline materials matter transport takes place along definite paths that define the mechanisms of sintering. The matter is transported from the regions of higher chemical potential (referred to as the source of matter) to regions of lower chemical potential (referred to as sink). There are at least six different mechanisms of sintering in polycrystalline materials. All of these lead to growth of necks between the particles. Neck growth produces bonding between particles, so the strength of the consolidated powder form increases during sintering. Only a few of the mechanisms, however, lead to shrinkage or densification. In these so called densifying mechanisms, matter is removed from the grain boundaries (mechanisms 4 and 5) or from dislocations within the neck region (mechanisms 1-3) are sometimes referred to as nondensifying mechanisms. The nondensifying mechanisms cannot simply be ignored. When they occur, they reduce the curvature of the neck surface (i.e., the driving force is sintering) and so reduce the rate of the densifying mechanisms.

Sintering provides inter particle bonding that generates the attractive forces needed to hold together the otherwise loose ceramic powder mass. To study sintering one monitors the density, surface area, shrinkage, or some other easily measured parameter
that correlates favourably with the sintered properties. Sintering is the result of atomic motion stimulated by high temperature. Diffusive processes generally are dominant. Several variables influence the rate of sintering. These include the initial density, material, particle size, sintering atmosphere, temperature, time and heating rate. The geometric progression associated with sintering can be divided into three stages: initial, intermediate and final. During the initial stage, particles form bonds at the particle contacts. As densification proceeds, new contacts will form; hence, there will be variations in the degree of sintering from point-to-point in the microstructure due to the delayed contact formation. With prolonged sintering, the pore structure becomes smoothened, leading to the intermediate stage, which corresponds to the open continuous pore structure that exists between densities of approximately 70 and 92% of theoretical values. In the intermediate stage, the sintering rate is continuously decreasing and is very sensitive to the pore-grain boundary morphology. Grain growth occurs in the later portion of sintering, during which the pores become spherical and isolated. Elimination of isolated pores is difficult at this point. The final stage of sintering corresponds to closed, spherical pores that shrink slowly by vacancy diffusion to grain boundaries. Such densification is sensitive to the relative grain size and the attachment of pores to grain boundaries, any atmosphere trapped in the pores will inhibit densification.

Several potential mass transport paths can be active during sintering. The characteristic distinction is between surface and bulk processes. Bulk transport provides densification, while surface transport contributes to inter particle bonding without densification. Because of complexities in the particle-pore geometry, mass transport processes and stages of sintering, it is typical to resort to computer simulations to quantify the sintering models. These simulations have actually predicted the behaviour of several systems. One major benefit is that they allow various processing options to be evaluated without the need for repetitive and painstaking laboratory measurements.

Additive phases that improve diffusion rates during sintering are used in many ceramic materials. These phases can be used to stabilize desirable crystal structures or, more typically, to form a liquid phase to increase the rate of sintering. Liquid-phase
Sintering is an attractive option for many of the high performance materials because of the rapid processing cycle, high final density and excellent final properties.

The atomic motion in sintering contributes to the formation of weld bonds between the particle and the elimination of pores. The sintered material exhibits improved strength and other properties. To enhance the overall process, external force (pressure) or chemical additives can be used.

Six distinct mechanisms can contribute to the sintering of a consolidated mass of crystalline particles: (1) surface diffusion (2) lattice diffusion (3) vapour transport (4) grain boundary diffusion (5) lattice diffusion from the grain boundary, and (6) plastic flow. Only mechanisms 1-3 lead to densification, but all cause the necks to grow and so influence the rate of densification. These six mechanisms are pictorially illustrated in figure 2.5.

![Diagram of sintering mechanisms](image)

**Figure 2.5** shows the six different mechanisms during sintering of the ceramic samples.

Particles sinter together by atomic motions that act to eliminate the high surface energy associated with an unsintered powder. The surface energy per unit volume is inversely proportional to the particle diameter. Thus smaller particles have more energy and sinter more rapidly than larger particles. However, not all of the surface energy is
necessarily available as a driving force for sintering. For a crystalline solid, nearly every particle contact will evolve a grain boundary with associated grain boundary energy. These grain boundaries prove important to atomic motion because the boundaries are defective regions with high atomic mobility.

During sintering, neck growth by the movement of mass to the neck is desirable because it reduces the surface energy by decreasing the total surface area. The structural changes associated with neck-growth depend on several possible transport mechanisms, most of which are diffusion processes. Diffusion is thermally activated meaning that there is minimum energy necessary for atomic or ionic movement and there must be available sites. This motion depends on the atoms or ions attaining energy necessary to break free from their present sites and moving into other available sites. The population of available sites and the number of atoms with sufficient energy to move into these sites both vary according to the Arrhenius temperature relation,

\[ \frac{N}{N_0} = \exp\left(-\frac{E}{kT}\right) \]  

(2.4)

where \( \frac{N}{N_0} \) is the ratio of available sites or activated atoms to total atoms, \( E \) is the appropriate activation energy, \( k \) is the Boltzmann constant, and \( T \) is the absolute temperature. Thus, sintering is faster at higher temperatures because of the increased number of active atoms and available sites.

The shrinkage, \( \Delta L / L_0 \), is the change in compact length from the initial dimension, \( \Delta L \), divided by the initial dimension, \( L_0 \). Because of shrinkage, the compact densities vary from the fractional green density \( f_g \) to the fractional sintered density \( f_s \) according to the relation:

\[ f_s = f_g (1 - \Delta L / L_0)^3 \]  

(2.5)

The densification \( \Psi \) is the change in density due to sintering divided by the change needed to attain a pore-free solid:

\[ \Psi = (f_s - f_g) / (1 - f_g) \]  

(2.6)
Densification, final density, neck size, surface area, and shrinkage are the related measures of pore elimination process during sintering. At high temperatures, sintering is more rapid; consequently shorter times are needed to attain an equivalent degree of sintering.

**Transport Mechanisms** are the methods by which mass flow occurs in response to the driving forces. The two classes of transport mechanisms are surface transport and bulk transport. These are composed of the actual atomistic mechanisms contributing to mass flow.

**Surface transport** involves neck growth without a change in particle spacing (no densification) due to mass flow originating and terminating at the particle surface. Surface diffusion and evaporation condensation are the two most important contributors during surface transport controlled sintering. Surface diffusion dominates the sintering of many covalent solids (such as pure boron and silicon carbide). Evaporation condensation is not as important, but is observed to dominate the sintering of low stability ceramics such as sodium chloride.

**Bulk Transport:** In contrast, bulk transport controlled sintering results in shrinkage. The mass originates at the particle interior with deposition at the neck. Bulk transport mechanisms include volume diffusion, grain boundary diffusion, plastic flow, and viscous flow. Plastic flow is usually not important for crystalline ceramics, because any dislocation motion would produce identical ionic neighbours, a condition that is undesirable. Also the stresses due to surface tension encountered during sintering are generally insufficient to generate dislocations. However, some transmission electron microscopy (TEM) observations indicate dislocation motion in the neck region due to the thermal stresses associated with rapid heating. In contrast, amorphous materials sinter by viscous flow, where the particles coalesce at a rate that depends on the particle size and material viscosity. Viscous flow is also possible for crystalline ceramics containing glass phases on the grain boundaries. Grain boundary diffusion is fairly important to densification for most crystalline materials and appears to dominate the densification of many common ceramics. Volume diffusion is often restricted by the defect structure in
the ceramic. In ionic substances, the mobility of the slower ion species dictates the sintering rate. While both surface and bulk transport processes give neck growth, the main difference is in density (or shrinkage) during sintering. Generally bulk transport processes are more active at higher temperatures. The actual behaviour is dependent on the materials, particle size, sintering stage, temperature, and several other process variables.

2.8 Mixed-Powder Sintering

Mixed powders provide flexibility in sintering because it is easy to change composition and because some unique composite microstructures are possible. Two types of sintered structures are possible from mixed powders.

- Solid solutions, which involve the homogenisation of the powder mixture by diffusional processes.
- Composites, which involve co-sintering two distinct phases.

*Homogenisation* during sintering is an alternative to forming compacts from chemically prehomogenized powders. Sintering of multiple component powder systems is more complex than sintering single component compacts because of the simultaneous phase reactions and homogenization effects. Diffusional levelling of the chemical concentration gradients is dominant early in the sintering cycle.

*Mixed-phase sintering* has some recognised problems. The compositional gradients require control of both time and temperature to ensure homogenisation. The degree of homogenisation $H$ is defined as the point to point chemistry variation, and it varies with diffusion rate and particle size as follows [4].

$$H \approx \frac{D \cdot t}{Y^2} \quad (2.7)$$

where $Y$ is the scale of the microstructural segregation, $D_{\alpha}$ is the volume diffusivity, and $t$ is the time. The scale of segregation as measured by $Y$ depends on the particle size and concentration of the powders. Equation 2.7 shows that homogenisation is faster with small particles where the diffusion distances are small. If the diffusion rates of the two
components are very different, then swelling may occur. The phase diagram is important to understanding the possible phase reactions during mixed phase sintering. Composites with two interlaced phases can be formed if a condition of co-sintering is attained [5]. Success in cosintering requires specific particle size ratios and uses of compositions that exhibit similar shrinkage versus temperature behaviours.

2. 9 Enhanced solid-state sintering

To provide the maximum desirable properties, it is often necessary to enhance densification. The common approaches are (i) phase stabilization (ii) Activated sintering (iii) Reactive sintering (iv) Liquid phase sintering, the details of each are outlined below [3].

Phase stabilization: Diffusivity of a material is determined by several factors, including temperature, crystal structure and defect configuration. The degree of sintering densification depends on the phases present at the sintering temperature. Additionally, mixed phase microstructures resist grain growth during sintering, especially in the intermediate stage. It is possible to adjust the composition or stoichiometry of a powder system to stabilize a phase with a high sintering rate. This can involve use of a second phase to pin grain growth during sintering [6].

Activated sintering: This allows for either a lower sintering temperature, a shorter sintering time, or improvement in properties from a chemical addition to the powder. One of the most dramatic examples of activated sintering occurs when tungsten or molybdenum are treated with certain transition metals. The successful additive action improve the rate of bulk transport during sintering by providing a fast diffusion path. To perform this role, the activator segregates to the inter particle contacts where it provides a high diffusivity, short-circuit path by forming a low melting temperature phase. The lower melting point ensures a lower activation energy for diffusion. Typically, an activator that decreases the liquidus and solidus of the base material is most successful. At temperatures slightly above the activated sintering range, a liquid phase forms. Formation of a liquid phase is another means of enhancing sintering.
**Reactive sintering**: Additives are also used to prevent stoichiometry loss during sintering. An excess of the higher stability species might be needed to avoid decomposition of the compound during sintering. Also surface contaminants may attack one of the constituents, leading to preferential attack or depletion. For this reason it is a common practice to add excess elemental constituents during sintering. There are special sintering situations where mass can be gained by the compact by reaction with the sintering atmosphere. The most common form of such processing involves the use of excess silicon and nitrogen atmosphere. In sintering, the silicon forms silicon nitride and the reaction product swells to fill the pore space. These latter techniques rely on chemical reactions during sintering, and the many variables of these approaches are generally known as reactive sintering.

A chemical reaction may also provide a driving force for sintering. The decrease in energy accompanying a chemical reaction can be much greater than the driving force provided by an applied stress, which is significantly greater than that provided by the surface curvature. The change in free energy accompanying a chemical reaction is given by:

$$
\Delta G^o = -RT \ln K_{eq}
$$

(2.8)

where $R$ is the gas constant (8.3 J/mol), $T$ is the absolute temperature, and $K_{eq}$ is the equilibrium constant for the reaction. Taking $T = 1000K$ and $K_{eq} = 10$, then $\Delta G^o \approx 20000J/mol$. In spite of very high driving force, a chemical reaction is not used deliberately to drive the densification process in advanced ceramics. As it is known, a major problem is that microstructure control becomes extremely difficult when a chemical reaction occurs concurrently with the sintering process. The driving forces provide a motivation for sintering. However, for sintering to occur, transport of matter must take place. In crystalline solids, matter transport occurs by a process of diffusion.

2.10 **Liquid phase sintering**

In two-phase systems involving mixed powders, liquid formation is possible because of differing melting ranges for the components or the formation of a low melting
phase (including a glass phase). In such systems, the liquid may provide for rapid transport and therefore rapid sintering if certain criteria are met [7]. The liquid must form a film surrounding the solid phase. Thus, wetting is the first requirement. Secondly, the liquid must have a solubility for the solid. Finally, the diffusive transport for the solid atoms dissolved in the liquid should be high enough to ensure rapid sintering. The formation of a liquid film provides the benefit of a surface tension force acting to aid densification and pore elimination. In this sense, the liquid phase acts like a low-pressure external stress. In liquid-phase sintering, the densification rate is much faster than in solid-state sintering, and times as short as 15 minutes at the maximum temperature can be successful in producing full density.

When a mixture of powders is heated, liquid forms and flows to wet the particles. The combination of wetting, liquid flow, and particle rearrangement all contribute to densification. With continued heating, the solid phase dissolves into the liquid and the amount of liquid grows until it is saturated with the solid component. The liquid phase then becomes a carrier for the solid-phase atoms in a process termed solution-reprecipitation wherein the small particles dissolve and reprecipitate on the large particles. This sequence of events do not significantly change the amount of liquid or solid. It does provide for densification and coarsening of the solid phase. Accordingly, the solid phase can achieve a higher packing density through particle shape accommodation which allows better packing [8]. Consequently, the sintered microstructure consists of contacting solid grains with an interspersed (solidified) liquid matrix. The solid grains exhibit shape accommodation, where flat faces occur on neighbouring grains, allowing them to fit into close proximity to one another. This releases liquid to fill the pore space.

Small particles aid densification in short sintering times. In general, coarsening is to be avoided because it degrades mechanical properties. Densification is also aided by large amounts of liquid and high solid solubilities in the liquid. At liquid content of approximately 35 Vol %, full density is achieved in the rearrangement stage and considerable compact slumping occurs. Consequently large amounts of liquid phase
cannot be used because the compact lacks sufficient rigidity during sintering to maintain its shape [9].

**Liquid phase sintering versus activated sintering**: Liquid phase sintering and activated sintering are similar densification enhancement techniques. Both involve the use of a second phase at the sintering temperature to provide rapid mass transport of an effective short-circuit path. A major difference between liquid phase and activated sintering is in the amount of second phase present at the sintering temperature. Liquid phase systems typically have several times more second phases. This is beneficial because the second phase is the continuous phase in the sintered product. Consequently, liquid phase sintered products often are more capable of sustaining strain and deformation, which lead to improved mechanical properties. A new and potentially useful variant is transient liquid phase sintering where liquid forms from mixed powders but persists only for a short time. This allows the liquid to induce densification without causing grain coarsening. Swelling can occur in some cases, even though the compact undergoes substantial strengthening.

**Supersolidus liquid phase sintering** is an alternative processing approach that relies on the use of prealloy (PA) powders [10]. This technique will be applicable to rapidly solidified and atomized ceramic powders. The powders are heated to a temperature at which a liquid phase nucleates within each particle. The approach is attractive because of the high densification possible with large particle sizes. In supersolidus liquid phase sintering, the temperature is held intermediate between the liquidus and solidus for the composition. As a consequence, the individual particles become mushy, and they can densify by capillary induced rearrangement with subsequent solution reprecipitation. The overall process is similar to viscous flow controlled sintering except that the liquid is formed within the particles rather than between the particles. Temperature and composition are the most important process variables because these variables dictate the volume fraction of liquid. The process can be applied to systems having large melting ranges. The principles of supersolidus liquid-phase sintering have sufficiently advanced that materials can be designed for the process. A first application in ceramics is for the densification of alumina-glass powder formed using plasma atomisation.
2.11 Preparation of strontium barium niobate ceramics

The raw materials SrCO$_3$, BaCO$_3$, Nb$_2$O$_5$ with 99.99% purity were used for the preparation of strontium barium niobate (SBN). The compound formation of SBN with tetragonal tungsten bronze type structure (TTB), is following the following the solid state reaction

$$x\text{SrCO}_3 + (1-x)\text{BaCO}_3 + \text{Nb}_2\text{O}_5 \rightarrow \text{Sr}_{x}\text{Ba}_{1-x}\text{Nb}_2\text{O}_6 + \text{CO}_2 (g) \quad (2.9)$$

Sr$_x$Ba$_{1-x}$Nb$_2$O$_6$ samples were prepared by weighing and mixing SrCO$_3$, BaCO$_3$, and Nb$_2$O$_5$ at the molar ratios of the compounds. Stoichiometric quantities of the reagents were first dry mixed in an agate mortar. The composition was further wet-mixed for 1 hour with a suitable organic solvent (methanol). The reaction mixture, after drying, was calcined at 800°C for three hours. The calcined powder was remilled for 1 hour, again in the presence of methanol. The calcined (800 °C/3 hours) powder was cold pressed into pellets (diameter = 10 mm, thickness = 10 mm) by applying a pressure $5 \times 10^3$ Kg/inch$^2$, after adding polyvinyl alcohol as binder, using the die. The density of the pressed green pellets are ~ 60% of the theoretical density. The disks were sintered at 1270 °C for 4 hours in air by keeping them on alumina crucible, in a high temperature programmable furnace. The furnace heating rate was set at 350-400 °C/hour. After attaining the set temperature, the soaking time was set for 4 hours, after which the furnace was allowed to cool to room temperature at the natural cooling rate. Just after removal from the furnace, under ambient conditions, the disks were white. These disks were found to change from white to dull yellow as a function of exposure time.

In this work we have prepared strontium barium niobate with different composition. The following are the list of SBN samples that have prepared for the present studies.

(1) Sr$_{0.75}$Ba$_{0.25}$Nb$_2$O$_6$  (2) Sr$_{0.61}$Ba$_{0.39}$Nb$_2$O$_6$  (3) Sr$_{0.60}$Ba$_{0.40}$Nb$_2$O$_6$
(4) Sr$_{0.55}$Ba$_{0.45}$Nb$_2$O$_6$  (5) Sr$_{0.50}$Ba$_{0.50}$Nb$_2$O$_6$  (6) Sr$_{0.47}$Ba$_{0.53}$Nb$_2$O$_6$
(7) Sr$_{0.45}$Ba$_{0.55}$Nb$_2$O$_6$  (8) Sr$_{0.43}$Ba$_{0.57}$Nb$_2$O$_6$  (9) Sr$_{0.40}$Ba$_{0.60}$Nb$_2$O$_6$
(10) Sr$_{0.35}$Ba$_{0.65}$Nb$_2$O$_6$. 
The quantity of each starting raw material is calculated, according to the molar ratios, in order to get 10 grams of end product for each sample.

The formation of SBN-60 (where \( x = 0.60 \)) as a function of temperature at heating rate of \( 10^3 \)°C/ minutes was reported to be at 1270 °C, where as 100% formation of SBN-50 for the same heating rate is 1200 °C [11]. The higher the heating rate, the higher the temperature that is required to attain the same fraction that has reacted to increases as the Sr: Ba ratio increases.

The reaction formation of strontium barium niobate seems to be diffusion controlled process. The higher the molar Sr: Ba ratio, the higher the activation energy that is necessary to form SBN. This is attributed to the distortion of the structure, which makes the inter diffusion of barium and strontium more difficult. In solid state reactions, the reactants are not mixed on an atomic level and therefore, must diffuse or penetrate into each other if the reaction is to start and propagate with in the solid phase. Thus space co-ordinates have a significant role during the reaction. There are two fundamental processes that are involved in a solid-state reaction, which are (i) the chemical reaction itself, and (ii) the transport of matter to the reaction zone.

2. 12 Preparation of \( [\text{Sr}_{0.61}\text{Ba}_{0.39}]_{4-2x}\text{Li}_{2+x}\text{Eu}_x\text{Nb}_{10}\text{O}_{30} \) and \( [\text{Sr}_{0.61}\text{Ba}_{0.39}]_{4-2x}\text{Li}_{2+x}\text{Nd}_x\text{Nb}_{10}\text{O}_{30} \)

The raw materials \( \text{SrCO}_3, \text{BaCO}_3, \text{Nb}_2\text{O}_5, \text{Li}_2\text{O}_3, \text{Eu}_2\text{O}_3, \text{Nd}_2\text{O}_3 \) and polyvinyl alcohol with 99.99% purity were used for the preparation of rare-earth modified strontium barium niobate ceramics. The conventional solid state reaction method was used for the preparation of europium doped SBN ceramic samples where the following chemical reaction was followed.

\[
0.61(4-2x)\text{SrCO}_3 + 0.39(4-2x)\text{BaCO}_3 + (2+x)/2 \text{Li}_2\text{O}_3 + (x/2) \text{Eu}_2\text{O}_3 + 5 \text{Nb}_2\text{O}_5 \rightarrow [\text{Sr}_{0.61}\text{Ba}_{0.39}]_{4-2x}\text{Li}_{2+x}\text{Eu}_x\text{Nb}_{10}\text{O}_{30} + \text{CO}_2 \ (g) \ (2.4)
\]

Here the values of \( x \) varies for each composition. The typical values that are chosen are \( x = 0.1, 0.2, 0.3, 0.4 \)and 0.5. Similarly for the preparation of neodymium doped SBN the following reaction is followed.
The required amounts of carbonates and oxides were taken on molar ratios and mixed in an agate mortar for 1 hour, in presence of excess methanol to improve the homogeneity and calcined at 800 °C for 4 hours in alumina crucibles. The mixture was reground and pelletised into thin discs at a pressure of $5 \times 10^3$ Kg / inch$^2$ using a hydraulic press, after adding a few drops of polyvinyl alcohol as binding agent. Finally they were sintered in alumina crucible at 1200 °C in air for 4 hours and the so formed discs were allowed to cool naturally. The sintered pellets were cut into thin discs of approximately 1 mm. Thickness, using a crystal cutter. The two faces of the thin discs were polished, for dielectric studies. For powder X-Ray studies the pellets are crushed to fine powders.

### 2. 13 Preparation of barium sodium niobate (BNN) and $\text{Ba}_{3-2x}\text{Na}_{4+x}\text{Nd}_x\text{Nb}_{10}\text{O}_{30}$

The polycrystalline samples of $\text{Ba}_4\text{Na}_2\text{Nb}_{10}\text{O}_{30}$, $\text{Ba}_3\text{Na}_4\text{Nb}_{10}\text{O}_{30}$ and $\text{Ba}_{3-2x}\text{Na}_{4+x}\text{Nd}_x\text{Nb}_{10}\text{O}_{30}$ were prepared by high temperature solid state reaction of stoichiometric mixtures of oxides and carbonates. High purity (99.9%) constituents of carbonates and oxides were weighed at their molar ratios, mixed in an agate mortar for 1 hour in the presence of excess of methanol to improve the homogeneity. The dried powders of the compounds were then calcined at 800 °C for 4 hours in an alumina crucible. The undergoing chemical process during solid state reaction are according to the following reactions.

\begin{align*}
0.61(4-2x)\text{SrCO}_3 + 0.39(4-2x)\text{BaCO}_3 + (2+x)/2 \text{Li}_2\text{O}_3 + (x/2) \text{Nd}_2\text{O}_3 + 5 \text{Nb}_2\text{O}_5 & \rightarrow \\
[\text{Sr}_{0.61}\text{Ba}_{0.39}]_{4-2x}\text{Li}_{2+x}\text{Nd}_x\text{Nb}_{10}\text{O}_{30} + \text{CO}_2 \ (\text{g})
\end{align*}

(2.5)

The calculated amounts of carbonates and oxides were taken on molar ratios and mixed in an agate mortar for 1 hour, in presence of excess methanol to improve the homogeneity and calcined at 800 °C for 4 hours in alumina crucibles. The mixture was reground and pelletised into thin discs at a pressure of $5 \times 10^3$ Kg / inch$^2$ using a hydraulic press, after adding a few drops of polyvinyl alcohol as binding agent. Finally they were sintered in alumina crucible at 1200 °C in air for 4 hours and the so formed discs were allowed to cool naturally. The sintered pellets were cut into thin discs of approximately 1 mm. Thickness, using a crystal cutter. The two faces of the thin discs were polished, for dielectric studies. For powder X-Ray studies the pellets are crushed to fine powders.

\begin{align*}
4 \text{BaCO}_3 + \text{Na}_2\text{CO}_3 + 5 \text{Nb}_2\text{O}_5 & \rightarrow \text{Ba}_4\text{Na}_3\text{Nb}_{10}\text{O}_{30} + \text{CO}_2 \ (\text{g}) \\
3 \text{BaCO}_3 + 2\text{Na}_2\text{CO}_3 + 5 \text{Nb}_2\text{O}_5 & \rightarrow \text{Ba}_5\text{Na}_2\text{Nb}_{10}\text{O}_{30} + \text{CO}_2 \ (\text{g}) \\
(3-2x) \text{BaCO}_3 + (4+x)/2 \text{Na}_2\text{CO}_3 + x/2 \text{Nd}_2\text{O}_3 + 5 \text{Nb}_2\text{O}_5 & \rightarrow \text{Ba}_{3-2x}\text{Na}_{4+x}\text{Nd}_x\text{Nb}_{10}\text{O}_{30} + \text{CO}_2
\end{align*}

(2.12) (2.13) (2.14)

where the values of $x$ chosen are 0.1, 0.3, 0.5, 0.6 and 0.8. The calcined powders were again mixed and powdered many times to get homogeneous fine powders. Finally,
cylindrical pellets of diameter 10 mm and varying thickness were prepared from the powders at a pressure of $5 \times 10^3$ Kg / inch$^2$ in a hydraulic press. The pellets were then sintered at 1200 °C in alumina crucibles for 4 hours. The furnace was allowed to cool naturally after sintering.

2. 14 References