CHAPTER 3

SYNTHESIS AND CHARACTERIZATION OF ZIRCONIA MINISPHERES

3.1 INTRODUCTION

In this chapter, studies on the preparation of zirconium oxalate gel and undoped zirconia minispheres by oxalate physical gelation technique using metal salt of chloride and oxalic acid have been reported. Possible reasons for the various stages of formation of the gel have also been explained. Results on characterization of zirconium oxalate sol and undoped zirconia minispheres have been presented in detail.

3.2 EXPERIMENTAL PROCEDURE

3.2.1 Selection of Materials

Preparation of stable zirconia sol was reported (Chang et al 1994) as a more difficult process as compared with other sols such as boehmite and titania because of the extremely rapid reaction of the zirconia alkoxide with water. This makes the synthesis of the zirconia sol very sensitive to experimental conditions and requires extreme carefulness. To avoid the above difficulties, an alternative way is to use zirconyl chloride octahydrate (ZrOCl₂·8H₂O) as a starting material to prepare undoped zirconium oxalate sol (ZO).
Easily water soluble metal salts of chlorides and nitrates have been selected since, the cost of the salts of inorganic starting material is quite cheap and hence the final product is cost effective as compared with the alkoxides. Moreover, metal alkoxides are relatively toxic and sensitive to moisture (Ju et al 1999). Following are the starting materials used for the present investigation:

1. Zirconyl chloride octahydrate, ZrOCl$_2$.8H$_2$O (CDH chemicals, India, LR Grade)
2. Oxalic acid dehydrate, H$_2$C$_2$O$_4$.2H$_2$O (SD fine chemicals, high purity)
3. Polyvinyl alcohol, PVA (CDH chemicals, India, AR Grade)
4. Yttrium nitrate hexahydrate, Y(NO$_3$)$_3$.6H$_2$O (CDH chemicals, India, AR Grade)
5. Magnesium nitrate hexahydrate, Mg(NO$_3$)$_3$.6H$_2$O (CDH chemicals, India, AR Grade)
6. Cerium nitrate hexahydrate, Ce(NO$_3$)$_3$.6H$_2$O (CDH chemicals, India, AR Grade)
7. Ammonia solution, NH$_3$ (CDH chemicals, India, AR Grade)

Triple distilled water has been used for the synthesis of the zirconium oxalate sol. All the metal salt solutions are used as such followed by filtration.

3.2.2 Preparation of Precursor Solutions

Clear solution of 1M concentration of the metal salt (ZrOCl$_2$.8H$_2$O) was prepared by mixing and dissolving them in triple distilled water in a glass container using a magnetic stirrer and Teflon coated paddle. Oxalic acid ((COOH)$_2$).2H$_2$O) was refluxed in triple distilled water at 60°C to obtain 1M concentration solution.
3.2.3 Preparation of Gel

Oxalic acid was then drop-mixed in zirconium-oxy chloride for 1: 0.7 vol/vol ratio with continuous stirring to obtain a transparent sol (Settu and Gobinathan 1996; Balasubramanian 1996). Sol-gel processing has the advantage of producing ultra fine zirconia minispheres of required size by extruding zirconium oxalate sol. Various potential sol precursors were investigated and characterized, the optimum being an aqueous sol made from hydrolysed zirconium oxalate (ZrO(COO)₂) (Wang et al 2001). With constantly stirred 1M solution of zirconyl chloride, oxalic acid solution was added slowly at room temperature (~29°C), which produced white flocculates and disappeared immediately. As the addition of oxalic acid was continued, a decrease in the rate of disappearance of white flocculates was observed and finally a white opaque gel appeared. As the stirring was continued, the gel thus yielded a clear sol. The formation of zirconyl oxalate (ZO) was also experimented by Oleg Vasylkiv and Yoshio Sakka (2000) for preparing nano-zirconia powders. The formed sol was transformed to a transparent thixotropic gel at room temperature by physical gelation. As the time increased, the clear gels again became slightly opaque. The addition of excess oxalic acid led to the formation of complete opaque sol.

The sol thus obtained was kept at room temperature for a very short time to acquire gelation. The viscosity of the sol was found to increase with time. The required viscosity could be obtained by adding a suitable binder polyvinyl alcohol PVA (35 wt%). The reaction can be better understood by the following equation (3.1):

\[ \text{ZrOCl}_2\cdot 8\text{H}_2\text{O} + (\text{COOH})_2\cdot 2\text{H}_2\text{O} \rightarrow \text{ZrO(COO)}_2 + 2\text{HCl} + 10\text{H}_2\text{O} \]  (3.1)
The HCl solution can be removed via centrifugation for an extended time and subsequent washing must be repeated not less than 8-10 times. Such a procedure was found to be inefficient for the minisphere preparation. The standard procedure of filtration could not be used effectively, because the oxalate particle size was 5-8 nm, depending on the water content in the precursor solution, which was too fine for the filter. Experimentally, it was proved by Oleg Vasylktiv and Yoshio Sakka (2000) that the surface area of the oxalate that was obtained under room-temperature conditions was only 10-20% larger than that of the powder processed at a temperature of 4°C. It was insisted that the processing at the lowest temperatures was not necessary.

3.2.4 Formation of Stabilized Zirconia Gel (DLVO theory)

Immediately after the oxalic acid solution is mixed with the zirconyl chloride at room temperature, white flocculates are formed due to the localized concentration of the ions and the flocculates disappear spontaneously. Their rate of disappearance decreases with the addition of oxalic acid and a white thick gel is obtained which on vigorous stirring, transforms into a clear sol. The probable reasons for the variation of the rate of disappearance of the flocculates may be the higher ionic concentration of the solution and an uneven distribution of the ions in the mixture. Vigorous stirring or shaking favours the even distribution of the ions and the adsorption of protons on the colloidal particles, thereby creating an electrical double layer and thus a clear sol is obtained. As time increases the clarity of the sol decreases slightly this may be due to clustering of the colloidal particles. It has also been noticed that the atmospheric conditions have a marked effect on the formation of the transparent sol, gel and gelation time. For example, if the humidity of the atmosphere is greater than 95%, the formed sol and gel are highly transparent at room temperature and the time taken for gelation is more; if the humidity is less than 90%, the formed sol is of aggregative nature.
and the gel is opaque. This may be due to the difference in the reaction rates for the formation of the sol and gel. However, a systematic study needs to be carried out to understand the effect of atmospheric conditions on sol and gel formation.

Though many forces influence the solutions, a possible qualitative explanation for the disappearance of the white flocculates at the beginning stage, formation of the white thick gel at the middle and the clear sol at the final stage can be discussed by means of DLVO theory based on the reference Li and Messing (1990). It may be consider that the formed hydrochloric acid is one of the reasons for the coagulation and the formation of the thick gel during the preparation of zirconyl oxalate gel (Etienne et al 1990). Conveniently, the existence of gelation stages may be classified as follows: the initial stage, where the formed white flocculates disappeared immediately after the oxalic acid is added with the mixed salt solution. The intermediate stage, where the continuous addition of the oxalic acid with the mixed solution of salts leads to white flocculates which, instead of disappearing, give rise to a white thick gel. In the final stage the observed white thick gel is slowly transformed to a clear transformed sol by continuous stirring/shaking.

According to the DLVO theory, a potential energy barrier exists between two colloidal particles. Depending on the magnitude of the barrier, particles may be either coagulated or dispersed. The total potential energy of the interaction between two particles can be described by the following equation (3.2):

\[ V_i = \frac{-\chi r}{12 H} + 2 \pi \epsilon \Psi^2 \exp (-\kappa H) \]  

(3.2)

where,  
\( r \) - Particle diameter  
\( \chi \) - Hamaker constant
H - Inter-particle separation
\( \varepsilon \) - Dielectric permittivity of the liquid medium
\( \Psi_o \) - Surface potential
\( \kappa \) - Debye-Huckel parameter

\[
\kappa = e z \sqrt{\frac{n}{K T \varepsilon}} \tag{3.2a}
\]

where,
K - Boltzmann constant
T - Temperature
e - Charge of an electron
z - Number of charges on a particle
n - Number of particles per unit volume

The energy barrier \( V_b \), using the equation (3.1), can be derived as:

\[
V_b = \frac{-\Lambda a \kappa}{12} + 2 \pi \varepsilon a \Psi_o^2 \tag{3.3}
\]

From the equation 3.3, it is clear that the value of the energy barrier decreases when the dielectric constant of the medium decreases. When the oxalic acid is added with the mixture of aqueous solutions of zirconyl chloride, the dielectric constant of the total system will decrease due to the formation of the hydrochloric acid which results in the disappearance of the white flocculates immediately. This may be due to the thickness of the electrical double layer which is explained on the basis of Figure 3.1. At low electrolytic concentration, the double layer term dominates at large separation, giving a maximum in the energy. The height of this energy barrier depends on the surface charge density and the electrolyte concentration. On the basis of the reaction, it is clear that 2M of hydrochloric acid is formed by the addition of 1M of oxalic acid with zirconyl chloride. While considering the entire solution system, at the initial stage, the addition of small amount of oxalic
acid with zirconyl chloride gives only a small amount of hydrochloric acid. This results in a very small decrease in the dielectric constant and hence the formed flocculates disappeared.

As the addition of oxalic acid with zirconyl chloride solution continues, the formation of hydrochloric acid is more, which further decreases the dielectric constant of the total system. The particles collide with sufficient kinetic energy, so that even though the like ionic repulsion is more, they stuck together and give rise to a thick colloidal gel as observed by Li and Messing (1990).

It can be seen from Figure 3.1b that at higher concentrations, the double layer term may decay so rapidly that the van der Waals attraction is still significant at a separation beyond the range of the repulsion, and the particles can reside in a secondary minimum (arrow in the Figure 3.1b). This gives a much weaker attraction, which could easily be overcome by shear. According to this, if the formed gel is continuously stirred/shacked, the thick white gel disappears slowly and gives a clear sol.

### 3.2.5 Preparation of Minispheres

Though the viscosity of zirconium oxalate gel increases with time, the required viscosity can be obtained by adding a suitable binder, namely polyvinyl alcohol (PVA (35 wt%)). Measurements on viscosity of the sol with time were analyzed by Brookfield viscometer (Figure 3.6). PVA was added to the sol to obtain the required viscosity for sphere formation and green body strength. The PVA was used as organic binder to prevent crack in drying process and improves green density of the minispheres.
Figure 3.1 Schematic plots of the energy of interaction between two surfaces across a polar Liquid (Electrical double-layer repulsion gives a positive contribution which decreases exponentially as surface separation increases (line 1); van der Waals attraction gives a negative term which is an inverse power law function of separation (line 3). The net energy (line 2) is given by the sum of these two) (Horn 1990)
Mixing of organic binder (PVA) to the zirconia sol should be carefully handled. Stability of the sol is quite sensitive to pH, ion concentration and other conditions. Insufficient amount of PVA can introduce cracks in the minispheres, while excessive amount may cause swelling. The suitable viscosity of sol for sphere formation was identified as 15cPs. A 500 ml beaker filled with 400 ml of ammonia solution (setting solution) was taken as gelation container. At the suitable viscosity, the PVA mixed sol was added drop by drop to a gelation container for the formation of uniform minispheres (Figure 3.2). The spheres were then dried at room temperature for 24 hours (Figure 3.3a). The dried minispheres were sintered at 1500°C for 5 hours with a heating rate of 5°C/min (Figure 3.3b).

Dehydration of zirconyl oxalate started at an early state of sintering.

\[ \text{ZrOC}_2\text{O}_4 \cdot \text{nH}_2\text{O} \rightarrow \text{ZrOC}_2\text{O}_4 + \text{nH}_2\text{O} \]  \hspace{1cm} (3.4)

The decomposition of zirconyl oxalate into CO started from the sintering temperature around 200°C as observed by Gangadevi et al (1980).

\[ \text{ZrO(COO)}_2 \rightarrow \text{ZrO}_2 + \text{CO} + \text{CO}_2 \]  \hspace{1cm} (3.5)

Around 470°C the crystallization of tetragonal zirconia was observed. Thixotropic behaviour of zirconia was also reported by Etienne et al (1990). The flow chart (Figure 3.4) shows the procedure for the preparation of zirconia gel and minispheres.

### 3.3 SINTERING MECHANISMS

Sintering Process plays a prominent role in the fabrication of ceramic grinding media. Almost all ceramic bodies must be sintered at elevated temperature to produce a microstructure with the desired properties.
The two main functions of sintering are a) the development of atomic bonding between the particles to provide strength and b) the elimination of porosity. Densification is essentially the removal of gas phase or pores which exist in the starting particulate compacts. This is done by heat treatment which results in a strong bounding between adjacent particles and is technically referred to as sintering.

Figure 3.2 Schematic diagram illustrating the minispheres formation using zirconium oxalate sol in the setting solution
Figure 3.3 Optical photograph of undoped zirconia minispheres
a) dried at 40°C   b) sintered at 1500°C (stabilizer added)
Ceria, Yttria and Magnesia were used at appropriate concentration for the preparation of stabilized zirconia minispheres (detailed explanations are presented in chapter 4, 5 and 6 respectively).

* Ceria, Yttria and Magnesia were used at appropriate concentration for the preparation of stabilized zirconia minispheres (detailed explanations are presented in chapter 4, 5 and 6 respectively)

**Figure 3.4** Flow chart for the preparation of ZO gel and zirconia minispheres
Before the sintering occurs, the following criteria must be fulfilled:

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

Diffusion and viscous flow are the primary mechanism for material transport. Heat is a source of energy and the gradient of energy for the material transport is formed due to surface tension and particle-particle contact. The driving force for these processes is provided by the consequent solid surface energy of the particles by the grain boundary energy. For complete densification, the grain boundary area must be half the original particle surface area.

The compacts are densified at temperatures where mass transport eliminates the voids or pores or the gas phase. Mass transport is driven by the excess free energy associated with the surface area of the ceramic particle. The difference in surface curvature where the particles touch (net negative curvature), relative to the rest of the surface of the particle (positive curvature), causes mass to “fill” the contact region between the particles. If the mass is removed from the particle centers, mass transport occurs, which will lead to shrinkage and densification. This process is known as sintering.

Sintering does not commonly begin until the temperature in the product exceeds one-half or two-half of the melting temperature, which is sufficient for significant atomic diffusion for solid state sintering or significant diffusion and viscous flow when a liquid phase is present or produced by a chemical reaction. For sintering to occur there must be a decrease in the free energy of the system. Grain growth during sintering changes the configuration of grain boundaries relative to the pores and less markedly influence the shrinkage rate; for uniformly distributed pores the shrinkage rate will increase as the grain size decreases. Shrinkage, grain growth, dimensional and
homogenization during liquid phase sintering of ceramics are influenced by
the presence of additives. However to accomplish the process within a
reasonable time, kinetics of the matter transport also has to be considered.
There are several paths by which solid-state sintering can occur. These paths
define the mechanisms of diffusion and hence the mechanisms of sintering.

Sintering mechanisms are different for polycrystalline and
amorphous materials. Polycrystalline materials sinter by diffusional transport
of matter, where the matter transport takes place along definite paths that
define the mechanism of sintering, whereas the amorphous materials sinter by
viscous flow. There are at least six different mechanism of sintering in
polycrystalline ceramics as shown in figure 3.5. All of these lead to neck
growth between the particles, thereby increasing the strength of the compacts
during sintering. Only certain of these mechanisms, known to densifying
mechanisms, however, lead to shrinkage or densification. In these
mechanisms, matter is removed from the grain boundaries (mechanism 4 and
5 of Figure 3.5) or from dislocation within the neck region (mechanism 6).
The mechanisms that do not cause densification (mechanism 1-3) are known
as non-densifying mechanisms. Even though they do not take part in
densification when they occur, they reduce the curvature of the neck (i.e. the
driving force for sintering) and hence reduce the rate of sintering. In
amorphous material, viscous flow leads to neck growth as well as to
densification. Mechanisms of sintering in polycrystalline and amorphous
solids are given in Table 3.1.

There are basically four different types of sintering processes. They
are solid-state sintering, liquid-phase sintering, viscous sintering, and
vitrification. The different mechanisms of sintering that occur for the different
types of sintering are shown in Table 3.2. These are distinguished by the
diffusive path involved. The mechanism of sintering has extensively studied
by Kingery et al (1976). They have demonstrated that the linear shrinkage, which takes place in the case of viscous flow mechanism, is a linear function of the time $t$, according to the formula (3.6):

$$\frac{\Delta L}{L} = \frac{(3\nu)}{4\eta r} t \tag{3.6}$$

where ‘$\nu$’ is the surface tension, ‘$\eta$’ is viscosity and ‘$r$’ is the particle size.

### 3.3.1 Vapour-Phase Sintering

In the vapour-phase sintering, the driving energy is the difference in vapour pressure as a function of surface curvature. The material in transported from the surface of the particles, which have a positive radius of curvature a relatively high vapour pressure to the contact region between the particles, which has a negative radius of curvature and a much lower vapour pressure. The smaller the particles, the greater positive radius of curvature and the greater the driving force for vapour-phase transports. Vapour-phase transport changes the shape of the pores, achieves bonding between the adjacent particles and thus increases the material strength and decreases permeability due to open porosity. However, it does not result in shrinkage and cannot produce densification. So it must be accompanied by other mechanisms that provide bulk material transport or transport of pores to external surface.

### 3.3.2 Liquid-Phase Sintering

Liquid-phase sintering involves the presence of a viscous liquid at the sintering temperature and is a primary densification mechanism for most silicate systems. The three factors that control the rate of liquid-phase sintering are,

1. Particle size
2. Viscosity
3. Surface tension
The viscosity and surface tension are affected strongly by composition and temperature. Liquid-phase sintering occurs 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 mechanisms such as,

1. Rearrangement of the particle to achieve better packing.
2. Increases in the contact pressure between particles, which increases
3. The rate of material transfer by solution/precipitation, creep and plastic deformation and vapour transport and grain growth.

The composition and processing temperature are chosen such that a small liquid phase forms but insufficient to remove the gas phase. Changes in grain shape are essentially required if full density is to be achieved.

3.3.3 Reactive –Liquid Sintering

Reactive liquid sintering is also referred to as transient liquid sintering. A liquid is present during sintering to provide the same types of densification driving forces as discussed for liquid sintering. However, the liquid either changes compositions or disappears as the sintering process progresses or after it is completed. Since the liquid phase is consumed in the reaction, the resulting material can have extremely good high temperature property and in some cases can even be used for temperatures above the sintering temperature. In order to achieve good reactive liquid sintering, the following steps have to be accounted:

1. to select starting powders or additives that go through series of chemical combination with one or more intermediate compounds being liquid and final compound being solid.
2. to use starting powder that will form a solid solution at equilibrium but will pass through a liquid stage if equilibrium is reached.

3. to liquid-phase sintering, cool to yield a glass at the grain boundaries and then heat-treated to crystallize the glass.

### 3.3.4 Solid-State Sintering

The type of sintering that is the simplest case, but the process being fairly complex is that of the solid-state sintering. In this type of sintering, the powders do not melt; instead, the joining of the particles and the reduction in porosity occurs through atomic diffusion in the solid-state. Solid-state sintering involves material transport by volume diffusion. Diffusion can consist of movement of atoms or vacancies along surface or grain boundaries or through the volume of the material.

The driving force for solid-state sintering is the difference in the free energy or chemical potential between the free surfaces of the particles and the points of contact between adjacent particles. In this process, no liquid-phase is formed at the heat treatment temperature. The densification is achieved only by the change in grain shape.

There are three stages of sintering. The various stages of sintering are listed in Table 3.3. The initial stage involves rearrangement of particles and initial neck formation at the contact point between each particle. The arrangement consists of a slight movement or rotation of adjacent particles to increase the number of points of contact. Bonding occurs at the points of contact where material transport occurs and where the surface energy is higher. This stage of shrinkage is valid upto 65% of theoretical density (TD).
1. Surface diffusion
2. Lattice diffusion (from the surface)
3. Vapor transport
4. Grain boundary diffusion
5. Lattice diffusion (from the grain boundary)
6. Plastic flow

**Figure 3.5** Six distinct mechanisms contributing to sintering
Table 3.1  Mechanisms of sintering in polycrystalline and amorphous solids

<table>
<thead>
<tr>
<th>Type of Solid</th>
<th>Mechanism</th>
<th>Source of matter</th>
<th>Sink of matter</th>
<th>Densifying</th>
<th>Non-densifying</th>
</tr>
</thead>
<tbody>
<tr>
<td>Poly crystalline</td>
<td>Surface diffusion</td>
<td>Surface</td>
<td>Neck</td>
<td></td>
<td>X</td>
</tr>
<tr>
<td></td>
<td>Lattice diffusion</td>
<td>Surface</td>
<td>Neck</td>
<td></td>
<td>X</td>
</tr>
<tr>
<td></td>
<td>Vapor Transport</td>
<td>Surface</td>
<td>Neck</td>
<td></td>
<td>X</td>
</tr>
<tr>
<td></td>
<td>Grain Boundary</td>
<td>Grain Boundary</td>
<td>Neck</td>
<td></td>
<td>X</td>
</tr>
<tr>
<td></td>
<td>Lattice Diffusion</td>
<td>Grain Boundary</td>
<td>Neck</td>
<td></td>
<td>X</td>
</tr>
<tr>
<td></td>
<td>Lattice Diffusion</td>
<td>Dislocations</td>
<td>Neck</td>
<td></td>
<td>X</td>
</tr>
<tr>
<td>Amorphous</td>
<td>Viscous Flow</td>
<td>Unspecified</td>
<td>Unspecified</td>
<td></td>
<td>X</td>
</tr>
</tbody>
</table>

Table 3.2 Different mechanisms of sintering

<table>
<thead>
<tr>
<th>Type of Sintering</th>
<th>Material Transport Mechanism</th>
<th>Driving Energy</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vapor-phase</td>
<td>Evaporation – Condensation</td>
<td>Difference in Vapor pressure</td>
</tr>
<tr>
<td>Solid-State</td>
<td>Diffusion</td>
<td>Difference in free energy or chemical potential</td>
</tr>
<tr>
<td>Liquid-phase</td>
<td>Viscous-Diffusion</td>
<td>Capillary pressure, Surface tension</td>
</tr>
<tr>
<td>Reactive liquid</td>
<td>Viscous flow, Solution-precipitation</td>
<td>Capillary pressure, Surface tension.</td>
</tr>
</tbody>
</table>
In the second stage of sintering, known as the intermediate stage, the size of the neck between particles grows. Porosity decreases and the centers of the original particles move closer together. This results in shrinkage equivalent to the amount to decrease in porosity. The grain boundaries begin to move so that one grain begins to grow while the adjacent is consumed. This allows further neck growth and removal of porosity. Most of the shrinkage occurs during this stage of sintering is valid upto 92% of theoretical density.

The third stage of sintering is referred to as final stage of sintering and it involves the final removal of porosity. For the maximum removal of porosity, the grain growth must be controlled.

Table 3.3 Different stages of sintering and process

<table>
<thead>
<tr>
<th>Initial Stage</th>
<th>Intermediate stage</th>
<th>Final stage</th>
</tr>
</thead>
<tbody>
<tr>
<td>Particle</td>
<td>Neck growth.</td>
<td>Much grain growth.</td>
</tr>
<tr>
<td>Rearrangement</td>
<td>Grain growth</td>
<td>Discontinuous grain growth</td>
</tr>
<tr>
<td></td>
<td>High shrinkage.</td>
<td>Grain boundary.</td>
</tr>
<tr>
<td>Neck formation</td>
<td>Pore phase continuous.</td>
<td>Pores eliminated.</td>
</tr>
</tbody>
</table>

A major consideration is that there are two ways of reducing the surface energy of the powder, namely, (i) densification and (ii) coarsening.

3.3.5 Densification

During the densification process, the size of the particles remains as such, but the surface energy is replaced by grain boundary energy and the shape of the particles changes. Densification involves removal of atom from grain boundaries and deposition of atoms on the most concave parts of the free surface. This can occur in initial and final stages of sintering by lattice diffusion or boundary diffusion.
3.3.6 **Coarsening Process**

In this process, the particles retain their original shape but they change in size by growing and hence reducing the surface area.

For the production of good ceramic bodies, the coarsening is suppressed and the densification process is enhanced by controlling the factors which affect these processes. For solid state sintering, the atoms at the contact point experience a pressure difference with respect to the neck region. Owing to the presence of grain boundary between the two spheres, atoms can diffuse away from the contact points.

The following are the major variables to be noted during heat treatment;

(i) Processing temperature.
(ii) Time for which this temperature is maintained.
(iii) Particle size of the ceramic powder
(iv) Composition of the system including the use of additives and atmosphere.
(v) Applied pressure for those cases where hot pressing is used.

Following are the mass transport mechanisms during sintering; boundary diffusion, lattice diffusion, viscous flow and plastic flow. Surface diffusion and evaporation-condensation are not effective in sintering process. A detailed explanation regarding the theory of sintering is clearly given by Somiya and Moriyashi (1990).
3.4 RESULTS AND DISCUSSION

3.4.1 Effect of Viscosity, pH and Chloride Ion Concentration

The viscosity of the zirconium oxalate sol was measured using Brookfield viscometer. By taking measurements at different rotational speeds, an indication of the degree of thixotropy of the sample was obtained. In Figure 3.6, minimum variation in viscosity of the sol is observed at higher values of rotational speed (above 80rpm). Sharp decrease in viscosity is evident for the rotational speed at around 40rpm. The above said variations are found to be common for almost all aging period of the sol. Gradual increase in the viscosity is recorded with increase in the aging periods from 15mins to 24 hrs. Maximum of 45cPs is obtained for the sol aged to 24 hrs for a rotational speed of 10rpm.

Viscosity of the sol plays a major role for the extrusion of minispheres in the setting solution. By trial and error method, the appropriate viscosity of the zirconium oxalate sol for the formation of uniform size and shape of the minispheres is identified as 15 cPs. The required viscosity can be obtained by adding binder (PVA) with 35wt% which subsequently improves the green body strength of the minispheres.

Figure 3.7 illustrates the pH variation with respect to ageing time. pH value of the sol varies from 1.2 to 2.3 which indicates that the acidity of the sol decreases gradually for the ageing time between 50 to 400 mins. pH of the sol used for the drop generation is 1.5 for the aging time less than 45 mins. But, Wang and Lin (1991) observed that the difference in pH used during the sol-gel processing of the ZrO₂ had no influence on the temperature stability of t-ZrO₂ product.
The gelation time as a function of chloride ion concentration is shown in Figure 3.8. It has been found that the gelation time has exponential character with the concentration of the chloride ion. As the concentration of the oxide powder (chloride ion) increases, the gelation time decreases which may be due to the increase in HCl content. The concentration of the chloride ions has been estimated by using the Volhard’s volumetric method. The gelation time has been calculated as the time taken for the formation of the clear sol to the gelation point. The approximate gelation point has been taken as that time for which the semi-rigid mass should not come out from the beaker when tilted. Variation of viscosity of the sol with pH on a specific rotational speed is experimented by gradually increasing the oxalic acid content (Figure 3.9).

![Graph showing viscosity variation with speed]

**Figure 3.6** Variation of viscosity of the zirconium oxalate sol with ageing time
At about pH 4, the suspensions are in flocculated state as long-range van der Waals interactions between particles dominate and the viscosity of the suspensions reaches its maximum value. Two pH ranges are observed with lower viscosity (Figure 3.9). Above pH 9, electrosteric forces make the particles apart from each other and the suspensions are in dispersed conditions. The electrostatic mechanism explains the dispersion of zirconia particles in extreme acid condition (pH 2).

![Figure 3.7 pH variation of the zirconium oxalate sol with ageing time](image)

**Figure 3.7 pH variation of the zirconium oxalate sol with ageing time**

### 3.4.2 Effect of Heating Rate, Surface Area and Density

In order to study the effect of heating rate on the sinterability, two types of heating rate have been adopted namely, slow (5°C/min) and fast (10°C/min) heating rates. From the Table 3.1, it is observed that the sintered density of the slow heating rate for undoped zirconia minispheres reaches around 89% of TD for a soaking period of 5 hours whereas the density of the fast fired samples reach only around 87% of TD for the same period of soaking.
Figure 3.8 Gelation time as a function of chloride ion concentration

Figure 3.9 Variation of viscosity of the zirconium oxalate sol with pH and rotational speed of the viscometer
The same trend has been observed for the samples with a soaking period of 3 hours also. It may be explained that the fast heating may lead to the entrapment of small amount of residual chlorine and carbon by existing pores because there may not be sufficient time to escape during sintering due to the closing of pores. It can be concluded that the fast heating rate always lead to the lower density due to the entrapment of the residuals by the pores while sintering at slow heating rate favours the elimination of the residuals.

There is very little difference in the densification of sintered samples with soaking time 3 and 5 hours. While comparing these results with the previous reports, indicates that a longer sintering time has no effect on the degree of crystallinity (Callon et al 2000).

Table 3.4  Effect of heating rate on the sintered density of the undoped zirconia minispheeres sintered at 1500°C

<table>
<thead>
<tr>
<th>Heating rate</th>
<th>Soaking period (hours)</th>
<th>Density (g/cc)</th>
<th>Theoretical density (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Slow(5°C/min)</td>
<td>3</td>
<td>5.21</td>
<td>88.46</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>5.27</td>
<td>89.47</td>
</tr>
<tr>
<td>Fast(10°C/min)</td>
<td>3</td>
<td>5.11</td>
<td>86.76</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>5.16</td>
<td>87.61</td>
</tr>
</tbody>
</table>

Oleg Vasylktiv et al (2001) observed some differences in the temperature regions of oxalate decomposition and crystallization on faster heating rate compared with the slow heating rate. It is observed that the completion of oxalate decomposition and the start of the crystallization stage are not separated in temperature and time and occur simultaneously at higher temperatures.
Specific surface area has been estimated for undoped ZO using BET technique with nitrogen. From the Table 3.5, it is found that the surface area of the sintered particles decreases as the firing temperature increases due to the increases of the crystallite size, which is also reflected in the XRD patterns.

Table 3.5 Variation of surface area of undoped zirconia as a function of sintering temperature

<table>
<thead>
<tr>
<th>Firing Temp. (°C)</th>
<th>Specific Surface area (m²g⁻¹)</th>
<th>Density (g/cc)</th>
<th>Average Crystallite Size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>450</td>
<td>85</td>
<td>4.58</td>
<td>8</td>
</tr>
<tr>
<td>550</td>
<td>66</td>
<td>4.66</td>
<td>9</td>
</tr>
<tr>
<td>700</td>
<td>40</td>
<td>4.98</td>
<td>15</td>
</tr>
<tr>
<td>850</td>
<td>35</td>
<td>5.15</td>
<td>16</td>
</tr>
</tbody>
</table>

3.4.3 Thermal Analysis

Figure 3.10 shows the TGA from room temperature to 1000°C of the undoped ZrO₂ minispheres dried at 40°C. It has been observed that there are two major weight losses of 14.23% and 34.64%. First weight loss is due to the dehydration of water and the latter corresponds to the thermal decomposition of organics with the simultaneous formation of amorphous zirconia. There are two more weight losses observed around 480 and 570°C which may be due to the releases of chlorine along with the simultaneous crystallization of zirconia. Table 3.6 shows the various thermal change processes for the ZO system.

From the DTA of the dried undoped zirconia minispheres (Figure 3.11), it is seen that there are three peaks in the temperature range 100
to 800°C. The first endothermic peak observed around 120°C is due to the dehyration of water as observed in the TGA curve. The second endothermic peak around 290°C is due to the decomposition of oxalate which is also observed in TGA. The amorphous zirconia crystallizes at 471°C in metastable tetragonal (t) phase and the shoulder around 750°C may be due to the transformation to a monoclinic (m) phase. This displacive phase transformation is martensitic, so that a smooth curve is observed rather than a pronounced peak. These phase changes are also clearly observed in the XRD pattern (Figure 3.12).

Table 3.6 Thermal analysis data for zirconia minispheres

<table>
<thead>
<tr>
<th>Thermal change</th>
<th>% wt loss observed at the end of each stage</th>
<th>Temperature range (°C)</th>
<th>Type of reaction</th>
</tr>
</thead>
<tbody>
<tr>
<td>Release of physisorbed water</td>
<td>14.23</td>
<td>30-180</td>
<td>Endothermic</td>
</tr>
<tr>
<td>Organic decomposition</td>
<td>34.64</td>
<td>239-380</td>
<td>Endothermic</td>
</tr>
<tr>
<td>Phase formation (or) crystallization</td>
<td>-</td>
<td>430-510</td>
<td>Exothermic</td>
</tr>
</tbody>
</table>

3.4.4 XRD Analysis

To study the crystalline nature of the undoped zirconia minispheres, X-ray diffraction analysis has been carried out (Figure 3.12). It has been observed that the undoped zirconia minispheres dried at 40°C are amorphous in nature. The metastable zirconia starts crystallizing when the dried undoped zirconia minispheres are sintered at around 450°C and retains partial tetragonal phase upto 600°C. Above this temperature, the monoclinic phase evolves and completes at 800°C and the minispheres crumbled totally on firing.
The strong covalent nature of the Zr-O bond within the ZrO$_2$ lattice favors a 7-fold coordination number, which is offered by the monoclinic crystal structure. As a result, monoclinic is the most stable crystal structure at room temperature for undoped ZrO$_2$.

Normally for pure zirconia, the tetragonal phase is stable above 1170°C. The occurrence of metastable tetragonal phase with small mean crystallite size below this temperature has been contributed by several factors. They include surface energy (Garvie 1965), chemical effects (Gutzov et al 1994), difficulty in nucleating the monoclinic phase (Tani et al 1983) and pH (Jada and Peletis 1989).

Among these, nucleation is thought to follow a phenomenon as “Ostwald’s step rule” (Grant 1969), which states that, when a substance exists in more than one modification, the least stable state occurs first. In the present case, amorphous zirconia might be considered as a higher modification which transforms to the tetragonal phase around 470°C and is less stable than monoclinic. The crystallization of amorphous ZrO$_2$ starts with the formation of tetragonal nuclei followed by conversion to the monoclinic phase, depending on the kinetic conditions and chemical environment.

3.4.5 Microstructural Analysis

From the SEM images, it is observed that the surface of the sphere is filled with cracks which may be due to the occurrence of phase transformation and followed by the volume expansion. The samples sintered at 800-1500°C are possessed with cracks and heterogeneity in microstructure (Figure 3.13) which causes the lower densification of the sintered undoped zirconia minispheres. This leads to a destructive effect on retention of minisphere shape and strength after sintering.
Figure 3.10 TGA curve for the undoped zirconia minispheres

Figure 3.11 DTA curve for the undoped zirconia minispheres
Figure 3.12 XRD patterns for undoped zirconia minispheres with different sintering temperatures
(t – tetragonal, m- monoclinic)
3.5 CONCLUSION

The subject discussion of the present chapter was the preparation route and characterization of undoped zirconia minispheres. Transparent, physical and thixotropic ZO gel has been prepared by oxalate gelation. Possible reasons for the various stages of the formation of the gels, by means of DLVO theory, have been explained. Sintering mechanisms of sintering in polycrystalline ceramics, various stages of sintering and their processes have been explained in detail.

Variations of viscosity and pH with ageing time for the zirconium oxalate sol have been analyzed. Results on undoped zirconia minispheres are discussed in detail. It is observed that the undoped zirconia transforms into complete monoclinic phase at around 800°C. The spheres are found with cracks due to the volume expansion occurred on the t-m transformation. This leads to a destructive effect on retention of minisphere shape and strength after sintering. Thus, it can be concluded that the use of pure zirconia minisphere as grinding media is curtailed due to extensive microcracking.
caused by the anisotropic volume expansion accompanying tetragonal to monoclinic transition.

In order to overcome these difficulties stabilizing the tetragonal phase is essential which could be attained by adding suitable stabilizing agent. In the subsequent chapters three types of minispheres namely ceria-, yttria-, and magnesia-, stabilized zirconia minispheres have been prepared and characterized and the reports are recorded in chapter 4, 5 and 6 respectively.