CHAPTER II

POWDER PROCESSING AND CHARACTERIZATION

2.1 INTRODUCTION

The science of ceramic powder processing technology dictates the superiority of the structural and functional applications of an end product. Ceramic processing involves four basic steps: (1) powder manufacturing, (2) powder preparation for consolidation, (3) consolidation to an engineering shape, and (4) densification/microstructural development in order to eliminate void spaces and produce the microstructure with optimal properties. Each step has the potential for introducing a detrimental heterogeneity which will either persist while processing further or will develop a new heterogeneity during densification and microstructural development (Lange 1989). Although various powder processing techniques are available for the production of ceramic powders, the best one is the technique which ends up (results) with relatively soft agglomeration, open porosity and less heterogeneity. Best homogenization of a ceramic powder can be obtained by means of a properly controlled colloidal preparation method.

The subject discussion of this chapter is about the various methods of powder processing techniques, a brief outline of the development of zirconia and the scope of the present problem. The methodology adopted for the preparation of zirconia and the results are discussed.
2.2 POWDER PREPARATION METHODS

The availability of fine homogeneous powders is important for the fabrication of modern ceramic structural as well as functional devices. Several powder preparation techniques are being used for both laboratory and large scale (industrial) production.

The powder processing techniques are generally classified as

1. conventional and
2. non-conventional

2.2.1 Conventional technique

In this technique, the powder preparation steps involved are mixing, calcining and grinding of coarse starting materials to make them acceptable for fabrication and for their subsequent sintering.

Harrison et al (1987) have prepared ultrafine tetragonal zirconia using sodium zirconate and sodium phosphate by means of solid state reaction at relatively lower temperature, 500°C. By impregnation of active carbon with zirconyl salt, a fully tetragonal zirconia fine powder of surface area 150 m²/g has been prepared (Ozawa and Kimura 1990) which was subsequently washed with water and calcined at 559°C to remove the carbon.

Production of zirconia from zircon was reported by Ayala et al (1992). They produced the m-zirconia in two ways, first by the decomposition of zircon with soda ash and second, with lime. Bhaduri et al (1988) have studied the possibility of fabrication of Ce-TZP material by conventional process.
2.2.2 Non-conventional technique

Non-conventional powder preparation technique does not involve any of the above steps. The powders obtained by this technique are:

* are highly homogeneous
* have desired composition and purity
* possess desired polymorphic form
* have required chemical and physical structure of surfaces

Based on the various processing steps involved, the following are the classification of the non-conventional preparation routes (Johnson 1985; Richerson 1992):

1. Sol-gel process
2. Precipitation technique
3. Liquid mixing route
4. Spray roasting and decomposition method
5. Freeze drying route
6. Hot kerosene drying technique
7. Hydrothermal method
8. Plasma route
9. Laser method

2.2.2.1 Sol-gel process

One of the non-conventional techniques, sol-gel method, is widely used for the preparation of highly sinteractive ceramic powders. Sol may be defined as the dispersed colloidal particles in a liquid. According to Flory (1986), a gel is an elastic solid with a very low modulus of elasticity. A detailed description regarding this process will be presented in a later section.
2.2.2.2 Precipitation technique

The precipitation technique involves precipitation of one or multiple metal cations with desired composition from the solution by changing the pH condition. This method is widely used in many industries to prepare oxide ceramic powders. The precipitates are first dried and then calcined at a desired temperature to obtain the final product. The properties of the powders prepared by this method can be changed or controlled by adjusting the pH, the reaction temperature and the surrounding atmosphere. Sometimes seed crystals are also used to nucleate and to maximize the final yield. For example, alumina can be prepared by the following route from aluminium nitrate.

\[
\text{Al(NO}_3\text{)}_3 + \text{NH}_4\text{OH} \rightarrow \text{Al(OH)}_3 + \text{NH}_4\text{NO}_3
\]

\[
2 \text{Al(OH)}_3 \rightarrow \text{Al}_2\text{O}_3 + 3 \text{H}_2\text{O}
\]

Haberko and co-workers (1975; 1979) have used the chloride process to prepare zirconia ultrafine powders. The influence of pH on the crystallization behavior of pure zirconia has been reported by Davis (1984). The metastable t phase was observed in the pH range from 3 to 4 and from 13 to 14. Monoclinic zirconia was produced in the range from 6.5 to 10.4. Benedetti et al (1990) have reported the role of Na\(^+\) ions on the stabilization of t (or) c phases of zirconia with respect to the variation in pH. The effect of pH on the formation of m and t phases of zirconia was reported by Adair and Denkewicz (1990) and Jada and Peletis (1989). In ZrO\(_2\) phase, the crystallization of m, t+m and t were observed at lower, middle and higher pH regions respectively.

Tsukuma and Shimada (1985) have prepared the Ce-TZP by hydrolysing the ZrOCl\(_2\) and CeCl\(_4\) to obtain fine powders. They studied the sinterability and mechanical properties of the Ce-TZP. By means of co-precipitation technique, Duh et al (1988b) have prepared zirconia with...
various mole% of CeO₂. They reported that 13.6 mole% of CeO₂-ZrO₂ solid solution has more stable t phase. Lucchini et al (1989) have prepared the Ce-TZP powders by hydrolysing the cerium nitrate and zirconyl chloride in the presence of urea.

Dolores and Paschoal (1988) have prepared the zirconia from ZrOCl₂ by the addition of (NH₄)₂SO₄ in a HCl solution. They have also analyzed the effect of sulphate ion on the precipitation of zirconium sulphate. Chatterjee et al (1989) have studied the suitability of the zirconium sulphate as a precursor for the preparation of zirconia. The presence of sulphate ions in the precipitates of hydrous zirconia affects the t phase of zirconia (Wu and Yu 1989; 1990). Aiken et al (1990) have prepared uniform spherical particles of zirconia from the precipitates of zirconium sulphate and zirconium carbonate by decomposition and the precipitates were prepared in the presence of urea.

Li et al (1989) have prepared zirconia particles with acicular morphology. By thermal decomposition of zirconium acetates, submicron zirconia powders with different morphology have been prepared by Bernstein et al (1989). Uchiyama et al (1987) have reported the preparation of Y₂O₃-stabilized zirconia from acetates of respective metals. The effect of several parameters such as concentration of starting solution, pH, choice of neutralizing agent and hydrolysing temperature were analyzed. Samdi et al (1988) have also prepared yttria-stabilized zirconia using metal salts of acetates.

Van de Graaf and Burggraaf (1984) have prepared zirconia powders by different routes and they have analyzed the sinterability and microstructure.
2.2.2.3 Liquid mix route

In this technique, a liquid containing the desired cations is mixed with any polymerizer which polymerizes when heated. While heating the cross-linked polymer, the solvent evaporates and gives the oxide powder. This process was pioneered by M. Pechini and is referred to either as Pechini process (Pechini 1967) or as amorphous citrate process (Eror and Anderson 1986; Marcilly et al. 1970).

In order to prepare the final powder, aqueous solutions of suitable cations are prepared and mixed with α-carboxylic acid to form a metal ion complex. Then polyhydroxy alcohol is added to undergo polyesterification when heated between 150 to 200°C. Heating is continued till 800°C to decompose the charred resin. The resultant residue is the required powder of fine size in the range from 20 to 50 nm. This process has been used to prepare mixed oxides and oxide solid solutions (Marcilly et al. 1970) of zirconia. Preparation of zirconia by using citric acid and metal alkoxide has been reported by Salze et al. (1986). The preparation of oxide powders has also been reported by using aqueous organo-metallic precursors. In this process the polyacrylic acid is reacted with multivalent ions in solution, forming a cross linked metal polyacrylate and is decomposed to get high quality oxide powders (Micheli 1989). From the organic zirconium complexes synthesized through SchifF's base and urea, the fine powder of zirconia was prepared by pyrolyzing the complex (Duricic et al. 1990).

2.2.2.4 Decomposition and spray roasting method

Spray roasting process involves spraying of solutions of precursor as atomized droplets into a hot chamber, which is at a desired temperature, to get the final product. Salt solutions of chlorides, nitrates etc are used in this process. The resulting powder consists of crystallite sizes ranging from 0.2 to 0.4 μm.
In the decomposition process, oxygen ions containing metal salts of nitrates (Yano et al. 1987), chlorides (Nonaka et al. 1989), sulfates and oxalates (Shi and Lin 1989) are used to prepare ceramic powders. These salts are calcined at elevated temperatures to obtain the corresponding metal oxide ceramic powders. Depending on the rate of decomposition, the properties of the final powders vary. Better results can be obtained by proper control of the rate of decomposition. Spray drying of hydrated zirconia and zirconyl chloride solution containing yttrium nitrate was also used to prepare yttria-stabilized zirconia powders (Chatterjee et al. 1992; Xiaming et al. 1993). Dubois et al. (1989) have reported the preparation of narrow sized yttria-stabilized zirconia by spray pyrolysis method.

2.2.2.5 Freeze drying route

Freeze drying process, also known as cryochemical processing, was first adopted by Schnettler et al. (1968) to prepare pure and homogeneous powders of uniform particle size. Droplets are made out of the solutions of metal ions of desired composition. These droplets are fed into a container which freezes the droplets rapidly. Water can be removed by vacuum sublimation and the resulting powder is calcined to obtain the final product.

2.2.2.6 Hot kerosene drying technique

Some powders which cannot be prepared by freeze drying can be prepared by hot kerosene drying. Appropriate cation containing solution is mixed with kerosene (1:1) and stirred vigorously with subsequent mixing of an emulsifying agent. This emulsion is metered drop by drop by a distilling apparatus into the well-stirred kerosene preheated to 170°C. The water evaporates instantly, leaving the homogeneous dry salt mixture dispersed in the kerosene. The salts are removed by screening and are thermally decomposed in air to get the oxides. Any liquid, which is in liquid state above 100°C is used for this purpose.
2.2.2.7 Hydrothermal method

Synthesis of ceramic powders by the hydrothermal method involves direct crystallization of composition in a hot, pressurized medium. Dawson (1988) has clearly explained this method of preparation. Normally, the temperature ranges from 100 to 350°C with pressures up to 15 MPa and the condition can be either oxidizing or reducing. The properties of the resultant powder such as particle size, surface area, etc can be controlled by incubation time, temperature and pressure. There is no need to heat treat the yield in order to obtain final desired powder. The resultant product itself is a fine single crystal. Morgan (1984) has synthesized the ultrafine 6 nm monoclinic zirconia powders by this method. A recently edited book on the hydrothermal process (Somiya 1989), clearly explains the preparation of various ceramic powders.

Clearfield (1964) has produced ultrafine nanosized zirconia by hydrothermal method. As per the surface free energy effects (Garvie 1965), formation of less than 12 nm sized particles of monoclinic zirconia is ruled out. However by the hydrothermal method it has been possible to prepare particles of less than this size. Mottet et al (1992) have reported that the morphology of hydrothermally prepared m-ZrO₂ depends on the specific mineralizers used. Hydrothermal method was used to crystallize the Ce-TZP in various organic solvents and water (Sato et al 1992). The powders prepared by this method showed better sinterability at low temperatures.

2.2.2.8 Plasma route

Various ceramic powders of high purity and very low particle size can be prepared by plasma method which is of two types, one is the dc arc jet system and the other is radio frequency induction system. There is no contamination in the latter type of plasma preparation because of the indirect transfer of energy to the reactor.
2.2.2.9 Laser method

Laser energy can also be used to prepare ceramic powders. The high energy of the laser is utilized to decompose the reactants which results in the final product. Purity is very high and the particle size is in the range of 5 to 20 nm. Powders such as SiC and Si₃N₄ have been synthesized successfully by this method.

2.2.3 Sol-gel process

Sol-gel technique, a non-conventional method, is used to prepare highly reactive ceramic powders which can be sintered at lower temperatures. The term sol generally refers to a mixture of solid colloidal particles (range 1 - 100 nm) in a liquid. Because of the small particle sizes, Brownian motion keeps colloidal sols stable against settling. Indeed, this definition of sol is suitable only for sol-gels in which colloidal suspensions are gelled through the surface forces to link the particles and thereby forming three dimensional network which gives the semi rigid mass called gel. There is another type of sol, called polymerized sol. In this type, the colloidal particles never exist. Since, the organometallic compound is partly hydrolyzed initially and then polymerized through chemical bonding, the term sol-gel can better be called as solution gelation. The formation of gels by the interaction of various forces is termed as physical gelation whereas the gel formation through the chemical polymerization is termed as polymerized gel. The gel may be defined as a mono, di or multi phasic semi rigid mass with high viscosity.

The advantages of the powders prepared by this method are

* molecular or atomic level mixing and hence homogeneity
* desired composition
* selective doping
Though the sol-gel method has many advantages, it also has its own disadvantages like high cost, time consuming, large shrinkage, health hazards of organic solutions etc. But considering the usefulness of the sol-gel prepared powders, the disadvantages can be ignored.

Although the usefulness of the sol-gel process is commercially limited for the preparation of the oxide powders, the preparation of glasses, dip coating, metal coating etc are explained in detail in the literature (Wenzel 1985; Dislich 1986). The usefulness of the sol-gel processed powders in thermal spraying is described by Wilson and Heathcote (1990). The processing of ceramic powders through non-conventional techniques is described recently by Segal (1989). Moreover the report of Mehrotra (1989) reveals the increasing trend of the sol-gel processing of various materials due to its various applications.

Classification of the sol-gel process is based on the nature of the formation of sol and gel (Partlow and Yoldas 1981; Johnson 1985).

The broad classification of sol-gel process is given in Figure 2.1 (Johnson 1985). This classification is based on the availability of starting materials and the characteristics of the sol and gel.

2.2.3.1 Polymerized alkoxides

To prepare single component oxide material using its corresponding alkoxide, first the alkoxide is partially hydrolyzed as given below,

\[ M(OR)_x + yH_2O \rightarrow M(OR)_{x-y} + yROH \]
Figure 2.1 Classification of sol-gel process
where R represents an alcoholic group, M is a cation. The partially hydrolyzed species are then allowed to form M-O-M linkage by a polymerization or condensation reaction. This type of continuous condensation leads to the formation of polymerized sol. Depending on the availability, cost or convenience, the polymerized alkoxide method is further subdivided into all alkoxide and alkoxide with metal salts.

For the preparation of multi metal oxides, powder from their respective alkoxide is allowed to hydrolyze partially and then mixed or both the alkoxides are mixed together and then allowed to hydrolyze to form the gel. Care must be taken while hydrolyzing the alkoxides, because the rate of hydrolysis is different for different alkoxides which may lead to heterogeneity in the final product.

Normally, the cost of the alkoxides is high. In order to reduce the cost to some extent, instead of choosing all components as alkoxides, the dopant may be chosen as one of its inorganic salts such as chloride or nitrate.

2.2.3.2 Colloidal sols

Sol-gels processed from colloidal sols best fit the common definition of a sol, a stable dispersion of colloidal particles in a liquid. The stability of the dispersed particles is due to the Brownian motion and various surface forces which are acting between the inter-particles. Normally, the dispersed ions or particles have $10^4$ times the concentration of the metals. Because of the inter-particle surface forces, a three dimensional network has been formed in the whole span of the sol which finally forms a semi rigid mass, called gel. This type of gelation is termed as physical gelation (Settu and Gobinathan 1994).
This category of sol-gel processing can be further classified as (i) the colloidal sols formed by a precipitation peptization and (ii) the colloidal sols formed by dispersion of very fine particulates.

In the precipitation peptization technique, first the metal ions are precipitated by adjusting the pH and then by repeated washing, the pH is brought down. Addition of small quantity of electrolyte with the washed precipitates facilitates the peptization of the precipitates. In the colloidal sols formed by dispersion of fine precipitates, the very fine calcined crystallites are dispersed by addition of dispersant.

2.3 PREVIOUS WORK ON THE PREPARATION OF ZIRCONIA BY SOL-GEL METHOD

In the present work only four types of materials, namely, pure Zirconia, Ceria-, Yttria-, and (Yttria, Ceria)-, doped Zirconia powders have been prepared and characterized. The subject discussion of this section is the preparation routes of these materials.

Though zirconia was found in the year 1789 from the Srilankan beach sand, extensive research has been started only after the seminal publication of Garvie et al (1975) on the stress induced phase transformation. Following this many researchers have intensively studied the various aspects of zirconia such as preparation by different routes, crystallization behavior, stabilization of metastable t phase to room temperature, sintering studies under various conditions, toughening mechanism, etc. In the subsequent text, the work carried out by various authors on the preparation and powder characterization of zirconia using sol-gel method is discussed.
2.3.1 All alkoxide route

Many reports are available on the preparation of zirconia and zirconia based ceramic powders by using alkoxides (Mazdiyasni et al 1965; 1967; Debsikdar 1986; Yoldas 1986). Mazdiyasni et al have reported the preparation of pure and yttria doped cubic zirconia by decomposition of metal alkoxide and they have analyzed the decomposition and crystallization behaviour. A transparent zirconia gel monolith was prepared from zirconium alkoxide (Debsikdar 1986) and it was subjected to pore size and size distribution analysis and surface area estimation. Yoldas (1986) has studied various factors which affect the condensation reaction such as type of alkyl group in the alkoxide, water/alkoxide ratio, molecular separation of species and the reaction temperature. These factors also affect the m→t transformation structure. Transparent zirconia gel monolith was prepared from alkoxide and 2-methoxy ethanol (Kundu et al 1988).

- Monodispersed powders of yttria (3 mole%-zirconia have been prepared (Uchiyama et al 1987; Bagley et al 1993) by hydrolysing the metal alkoxides. Effect of synthesis conditions such as ageing, water concentration and reflexing of the alkoxide solutions on powder preparation has been analyzed. Each particle derived by this method has almost equal concentration of yttria. Preparation of spray quality powder of high purity yttria-stabilized zirconia has been reported by Sherif and Shyu (1991) from emulsion hydrolysis of metal alkoxides, acetates and mixture of these two. By varying the experimental conditions, spherical or granular powders with particle size ranging from submicron to hundred micron were obtained. Hydrolysis of zirconia tetra-n-butoxide in 2-proponol yields monodispersed sol containing 4 nm sized particles (Okubo and Nagamoto 1995) and their subsequent sintering results only a few tens of nanometer sized grains.

Nagarajan and Rao (1991) have reported the preparation of 5 mole% of CeO₂-zirconia by hydrolysing the alkoxides.
2.3.2 Colloidal preparation

Shi and Lin (1989) have prepared zirconium dioxide powder by the precipitation method by using oxalic acid under various conditions. They have analyzed decomposition and crystallization behaviour of the precipitated powders. Pure monoclinic zirconia was prepared by mixing the chloride salt of zirconium and oxalic acid which results in the formation of zirconyl oxalate gel and decomposing it at 850°C (Etienne et al 1990). Gongyi and Yuli (1992) have prepared Y-TZP powders by oxalate precipitation in ethanol solution with various pH values. Gangadevi et al (1980a; 1980b) have also reported the preparation of zirconyl oxalate precipitates and they have studied the thermal decomposition behaviour of oxalates.

Using sol-gel method, Dayal et al (1989; 1992) have prepared Y-TZP with different compositions and they have studied the basic characteristics. Sol-emulsion-gel method has been used to prepare the zirconia at <140°C from zirconyl nitrate (Ramamurthi et al 1990).

Chatterjee and Ganguli (1986) have reported the preparation of pure and (MgO, CeO₂) doped zirconia by three routes, namely alkoxide, gel formation and spray drying. By using these powders, they have studied the crystallization behaviour.

2.4 SCOPE OF THE PROBLEM

From the foregoing discussion, it can be observed that pure zirconia and various stabilized zirconias are prepared mostly by using the precipitation method, sol-gel process (parent materials are mostly metal alkoxides), spray pyrolysis route, hydrothermal technique and citrate process. The reports available on oxalate gel derived powders are limited. Etienne et al (1990) have prepared pure zirconia using oxalate gelation
method. They have not prepared the doped zirconia and analyzed their sintering and mechanical behavior. Shi and Lin (1989) have studied only the preparation of zirconium dioxide powder by oxalate precipitation method. Gongyi and Yuli (1992) have prepared Y-TZP powders by oxalate precipitation in ethanol solution with various pH values. Hence, in this work, detailed studies on the preparation of pure zirconia, 10 mole\% of CeO$_2$-ZrO$_2$, 5 mole\% of Y$_2$O$_3$-ZrO$_2$, 4 mole\% of Y$_2$O$_3$-7 mole\% of CeO$_2$-ZrO$_2$, by oxalate physical gelation, using metal salts of chlorides, nitrates and oxalic acid in triple distilled water and their characterization have been reported.

2.5 EXPERIMENTAL PROCEDURE

2.5.1 Choice of materials

Very easily water soluble metal salts of chlorides and nitrates have been selected because compared with the alkoxides, the cost of the salts of inorganic starting materials is quite cheap and hence the final products are cost effective. 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. Yttrium nitrate hexahydrate, Y(NO$_3$)$_3$·6H$_2$O (CDH chemicals, India, AR Grade)

3. Cerium Nitrate hexahydrate, Ce(NO$_3$)$_3$·6H$_2$O (CDH chemicals, India, AR grade)

4. Oxalic acid dihydrate, H$_2$C$_2$O$_4$·2H$_2$O (SD fine chemicals, high purity)
Triple distilled water has been used throughout the experiments. All the metal salt solutions were used as such except filtration.

2.5.2 Preparation of precursor solutions

1M concentration of clear solutions of metal salts were prepared by mixing them with water in a glass container using a magnetic stirrer and teflon coated paddle. Oxalic acid solution was also prepared similarly.

2.5.3 Preparation of gels

2.5.3.1 Zirconyl oxalate (ZO) gel

With the constantly stirred 1M solution of zirconyl chloride, oxalic acid solution (1M) was added slowly at room temperature (~27°C), which produced white flocculates and disappeared immediately. As the addition of oxalic acid is continued, the rate of disappearance of white flocculates decreases and finally gives a white opaque gel. As the stirring/shaking is continued, the gel thus formed yielded a clear sol. The formed sol was transformed to a transparent thixotropic gel at room temperature by physical gelation. As the time increases, the clear gel again became slightly opaque. The addition of excess oxalic acid led to the formation of opaque gel.

2.5.3.2 Cerium-zirconyl oxalate (CZO) gel

Solutions of zirconyl chloride (1M) and cerium nitrate (1M) were thoroughly mixed together. An appropriate amount of oxalic acid was added with continuously stirred mixed solutions of metal cations at room temperature. During the formation of the CZO sol and gel, the observed characteristics were the same as that of the pure ZO system. The CZO gel was prepared in such a way that the final product of the calcined powder contains 10 mole% of CeO$_2$-ZrO$_2$. For this system, the molar ratio of (ZrO)$^{2+}$ to (C$_2$O$_4$)$^{2-}$ is 1.
2.5.3.3 Yttrium-zirconyl oxalate (YZO) gel

1M aqueous solutions of zirconyl chloride and yttrium nitrate were mixed together (corresponding to 5 mole% of $Y_2O_3$- $ZrO_2$ in the final calcined oxide powder). A desired quantity of oxalic acid solution (1M) was slowly added with the mixed solution of cations of yttrium and zirconium. The characteristics of the formation of YZO sol and gel were similar to those observed for the ZO system. However, the transparency of the sol and gel were found to be slightly opaque as compared with that of the CZO sol and gel.

2.5.3.4 Yttrium-cerium-zirconyl oxalate (YCZO) gel

1M aqueous solution of cerium nitrate was thoroughly mixed with the 1M solution of zirconyl chloride. With this mixed solution, 1M solution of yttrium nitrate was added. This solution is stirred for thorough mixing. The cations solution is prepared in such a way that the final calcined powder contains 4 mole% of $Y_2O_3$-7 mole% of $CeO_2-ZrO_2$. During the formation of YCZO sol and gel, the observed characteristics were found to be the same as that of the previous systems. However, the transparency of the sol and gel was higher than the YZO system.

The prepared gels were oven dried at 40°C and crushed in a mortar and pestle. The powders were calcined at 245, 425, 460, 600, 700 and 850°C for 1 hr to study the nature of the crystallization by means of powder X-ray diffraction and to estimate the surface area. Thermal behavior and IR studies of the dried gel powders were also performed.

The flow chart (Figure 2.2) shows the preparation procedure for these gel powders and their characterization.
For the preparation of CZO, YZO and YCZO gels their respective metal salt solutions were mixed with the zirconyl chloride solution.

* Figure 2.2 Flow chart for the gel preparation and characterization
2.6 RESULTS AND DISCUSSION

2.6.1 Formation of gels

When the oxalic acid solution is mixed with the zirconyl chloride solution at room temperature (~27°C), white flocculates are formed immediately due to the localized concentration of the ions and the flocculates disappear spontaneously. If the addition of oxalic acid continues, the rate of disappearance of the flocculates decreases and finally a white thick gel is obtained. After vigorous stirring/shaking of the gel, a clear sol is obtained. Probable reason 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. Vigorous stirring/shaking favors the even distribution of ions and the adsorption of the protons on the colloidal particles and thereby creating an electrical double layer. As time increases, the clarity of the sol slightly decreases which may be due to the 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 more than 95%, the formed sol and gel are highly transparent at room temperature and the time taken for gelation is more and 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 reason that the rate of reaction for the formation of the sol and gel is different. However, a systematic study has to be carried out to understand the effect of the atmospheric conditions on the formation of the sol and gel.

The CZO, YZO and YCZO gels have been prepared by the slow addition of oxalic acid with the mixed cation solutions of their respective salts with continuous stirring. The observed characteristics of these gels during the preparation are similar to that of ZO gel. The addition of stoichiometric ratio of oxalic acid with the mixed cations solution leads to the formation of an unclear sol which then turns out to be a white opaque
gel, on the other hand a transparent sol and gel have been observed when
the addition of oxalic acid is sufficient to form the zirconyl oxalate gel alone,
i.e., the ratio of (ZrO)_{2+} to (C_{2}O_{4})^{2-} is equal to 1M for all the CZO, YZO and
YCZO gels. However, the time taken for the formation of clear CZO and
YCZO sol is lower than that of the ZO and YZO sol. Moreover, the nature
of the transparency of sol and gel is higher for the CZO and YCZO compared
to that of ZO and YZO.

The cerium and yttrium ions are mixed in the form of their
respective nitrate salts. The nature of the dopants in the zirconyl oxalate gel
structure is not clearly understood. As suggested by Tohge et al (1984) for
the preparation of doped glasses, here also it is believed that the dopants
are uniformly distributed on the pore surface of the zirconyl oxalate gel
structure. During calcination the dopant ions are substituted for zirconium
ions in the crystal structure which favors the formation of the stabilized
zirconia. For a clear understanding, a detailed analysis has to be carried out
to study the effect of the temperature, atmospheric humidity and the
concentration of the solution on the formation of the sol and gel.

Though many forces influence the solutions (Horn 1990), 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 references Li and Messing (1990) and Horn (1990). Conveniently, the
existence of these three 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 solutions. 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, gives rise to a
white thick gel. In the final stage the observed white thick gel is slowly
transformed to a clear transparent sol by continuous stirring/shaking.
It may be considered that the formed hydrochloric acid is one of the reasons for the coagulation and the formation of the thick gel during the preparation of pure zirconyl oxalate gel, which is given by the following equation (Etienne et al 1990).

$$\text{ZrOCl}_2 + \text{H}_2\text{C}_2\text{O}_4 \rightarrow \text{ZrOC}_2\text{O}_4 + 2\text{HCl} \quad (2.1)$$

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:

$$V_T = \frac{\chi r}{12H} + \frac{2\pi e r \psi_o^2}{H} \exp(-\kappa H) \quad (2.2)$$

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

$$\kappa = \frac{e z \sqrt{n}}{K T \varepsilon}$$

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 (2.1), can be derived as:

$$V_b = \frac{-A\kappa a}{12} + 2\pi \varepsilon a \psi^2_o$$

(2.3)

From the equation 2.3, 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 mixed aqueous solutions of zirconyl chloride and yttrium or cerium nitrate, the dielectric constant of the total system will decrease due to the formation of the hydrochloric acid which results in the disappearance of the formed white flocculates immediately. This may be due to the thickness of the electrical double layer which is explained on the basis of Figure 2.3.

From the Figure 2.3a, at low electrolytic concentration, the double-layer term dominates at large separations, 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 causes further decrease in dielectric constant of the total system. Though the like ionic repulsion is more, the particles collide with sufficient kinetic energy, in that they can stick together and give a thick colloidal gel as observed by Li and Messing (1990) in the preparation of zirconia spherical particles.
Figure 2.3 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).
It can be seen from Figure 2.3b 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 1.3b). This gives a much weaker attraction, which could easily be overcome by shear. According to this, if the formed gel is continuously stirred/shaked, the thick white gel disappears slowly and gives a clear sol.

2.6.2 Preparation of concentrated sol

The preparation method of sol 1 (for the ZO, CZO, YZO and YCZO) has been clearly discussed in the earlier section. The gel which has been formed by the gelation of sol 1 is oven dried at 40°C. The powder obtained from the dried gel is slowly added with water with continuous stirring. The powder slowly dissolves in water which gives a sol, namely sol 2, which is more clear than the sol 1. The quantity of water taken for the preparation of sol 2 is same as that of the sol 1. This has been repeated for a number of times. As given in the equation 1, hydrochloric acid which is formed during the reaction of the reactants, plays an important role in the repetitization of the dried gel powder and the formation of the more clear gel by the sol 2. Along with the chloride ions the nitrate ions are also responsible for the repetitization of the dried gel powders in the systems CZO, YZO and YCZO. The adsorption of the positive charges on the surfaces of the particles may be the reason for the repetitization of the dried gel powder (Turner 1991).

The different stages of gelation and cycling processes are given in the chart (Figure 2.4).

The gelation time as a function of chloride ion concentration for the sol 1 and sol 2 is shown in Figures 2.5 to 2.8. It has been found that for sol 1 and 2 of the systems ZO and CZO, the gelation time has exponential character with the concentration of the chloride ion whereas for YZO and
For the preparation of repeatized CZO, YZO and YCZO gels corresponding cation solutions were mixed with the zirconyl chloride solution and the rest of the procedure is same as that of the ZO system.

Figure 2.4 Preparation flow chart for the concentrated sols
Figure 2.5 Gelation time as a function of concentration of chloride ion for sol 1.
Figure 2.6 Gelation time as a function of concentration of chloride ion for soil.
Figure 2.7 Gelation time as a function of concentration of chloride ion for sol 2.
Figure 2.8 Gelation time as a function of concentration of chloride ion for sol 2.
YCZO systems the sol 1 has an exponential character with the chloride ion concentration and the sol 2 has linear character with the chloride ion concentration. As the concentration of the oxide powder (chloride ion) increases, the gelation time decreases. The concentration of the chloride ions in sol 2 has been estimated by using the Volhard's volumetric method. The gelation time has been calculated as the time taken from the formation of 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.

It is possible to increase the concentration of the oxide powder in the sol 2 using the dried gel powders which are obtained from the gel of sol 1. The sol 1 of the ZO, CZO, YZO and YCZO contains 6.12, 6.67, 5.81 and 6.17 wt.% of their respective oxide powders. For the same wt.% of the respective powders, the gelation time for the repeptized sol 2 is higher than that of the sol 1. This may be due to the removal of the excess of hydrochloric acid that has been formed during the reaction of the reactants. It has been observed that the wt.% of the oxide powder can be increased upto 10 wt.% for the ZO, CZO and YCZO powder in the sol 2 whereas the wt.% of YZO in sol 2 cannot be increased due its high viscous nature. There is a difference in gelation time observed for the sol 2 of the ZO, CZO, YZO and YCZO systems. This may be due to the observed difference in viscous nature of their respective repeptized sols. The observed large difference in gelation time for the sols 1 and 2 lies in the total concentration of the ions. In the repeptized sol, due to the removal of the excess hydrochloric acid, during drying, favors the reduction of the total concentration of the ions in the sol 2 and hence the increase in the thickness of the electrical double layer which is the cause for the increase in gelation time.
2.6.3 Crystallization behavior

To study the crystalline nature of the prepared dried gel powders and calcined powders, X-ray diffraction analysis has been carried out. Figures 2.9 to 2.12 show the X-ray powder diffraction patterns for the dried and calcined powders of ZO, CZO, YZO and YCZO gels at 40°C and at different temperatures for 1 hr., respectively. It has been observed that all the precursors dried at 40°C are amorphous in nature. The metastable zirconia starts crystallizing when the dried powder of the ZO is calcined at 425°C and it retains the tetragonal phase up to 600°C (Settu et al. 1993). Above this temperature the monoclinic phase evolves and completes at 850°C.

Normally, the tetragonal phase is stable above 1170°C, but the occurrence of a metastable tetragonal phase with small mean crystallite size below this temperature is not well understood at this time and has been attributed to several factors. They include surface energy (Garvie 1965), chemical effects (Srinivasan and Angelies 1986; Srinivasan et al. 1990; 1992; Gongyi and Yuli 1992; Gutzov et al. 1994), difficulty in nucleating the monoclinic phase (Butler and Heuer 1982; Tani et al. 1983b), pH (Davis 1984; Jada and Peletis 1989), H₂SO₄ (Wu and Yu 1990) and Na⁺ ions (Benedetti et al. 1990). Among these, nucleation is thought to follow a phenomenon termed 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 425°C and is less stable than the monoclinic phase. A recent investigation (Yanwei et al. 1995) on the crystallization of metastable t phase of zirconia reveals that the topological structure of amorphous zirconia bears more resemblance to m-ZrO₂ structure than to the t-ZrO₂. The crystallization of amorphous ZrO₂ starts with the formation of monoclinic nuclei followed by their further growth or conversion to the t phase, depending on the particular kinetic conditions and chemical environment.
Figure 2.9 X-ray diffraction pattern as a function of heat treatment for dried ZO gel powder (calcination time 1 hr.).
Intensity of heat treatment for dried CZO gel powder (calcination time 1hr.).

Figure 2.10 X-ray diffraction pattern as a function of heat treatment for dried CZO gel powder (calcination time 1hr.).
Figure 2.11 X-ray diffraction pattern as a function of heat treatment for dried YZO gel powder (calcination time 1hr.).
Figure 2.12 X-ray diffraction pattern as a function of heat treatment for dried YCZO gel powder (calcination time 1hr.).
At 700°C both tetragonal and monoclinic phases exist. The tetragonal phase has been completely transformed to monoclinic phase when calcined at 850°C. The tetragonal phase starts to crystallize at 425°C and the X-ray patterns for 600°C and 850°C show the retention of stabilized tetragonal phase for the CZO gel. A recent study (Li et al. 1994) on the role of stabilization of the t phase of zirconia by Ce$^{4+}$ ions shows that the presence of these ions reduce the over crowding of the oxygen around the zirconium ion and hence relieve the strain energy associated with it. At 460°C, YZO and YCZO dried powders start crystallizing in the tetragonal phase. For calcination temperatures of 600°C and above, the retention of the tetragonal phase has been observed for these systems. The increased crystallite size with increase of calcination temperature is reflected in Figures 2.9 to 2.12 as the decrease in the width of the spectral lines.

To identify, whether the formed phase is tetragonal or cubic for the systems YZ and YCZ, higher angle X-ray diffraction (insert in the Figures 2.11 and 2.12) patterns have been recorded for both the powders calcined at 850°C for 1 hr. The insert in figures shows the existence of the tetragonal and cubic phases. These are identified from the reflections (004)$_t$, (004)$_c$ and (400)$_t$. Table 2.1 shows the crystallization of the different phases for these compounds at various calcination temperatures.

The lattice parameter values of pure and doped zirconias are given in Table 2.2. From the Table 2.2, it is clear that c/a ratio is lower for the YZO and YCZO systems than the CZO system which suggest the stability of t phase is more for the YZO and YCZO systems than the CZO system.

2.6.4 Thermal analysis

Weight loss and phase transition behavior of dried ZO, CZO, YZO and YCZO gels have been carried out by TGA and DTA studies (For all TGA and DTA, heating rate = 10°C/min.; Atmosphere = Air).
Table 2.1

Phase formation as a function of calcination temperature(°C)

<table>
<thead>
<tr>
<th>Sample</th>
<th>240</th>
<th>350</th>
<th>425</th>
<th>460</th>
<th>600</th>
<th>700</th>
<th>850</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZO</td>
<td>A</td>
<td>A</td>
<td>t</td>
<td>t</td>
<td>t</td>
<td>t &amp; m</td>
<td>m</td>
</tr>
<tr>
<td>CZO</td>
<td>A</td>
<td>A</td>
<td>t</td>
<td>t</td>
<td>t</td>
<td>t</td>
<td>t</td>
</tr>
<tr>
<td>YZO</td>
<td>A</td>
<td>A</td>
<td>-</td>
<td>t</td>
<td>t</td>
<td>t</td>
<td>t &amp; c</td>
</tr>
<tr>
<td>YCZO</td>
<td>A</td>
<td>A</td>
<td>-</td>
<td>t</td>
<td>t</td>
<td>t</td>
<td>t &amp; c</td>
</tr>
</tbody>
</table>

A = Amorphous; m = Monoclinic; t = Tetragonal; c = cubic

Table 2.2

Lattice parameter values of pure and doped zirconias

<table>
<thead>
<tr>
<th>System</th>
<th>Parameters</th>
<th>Angle Degrees</th>
<th>c/a ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>a nm</td>
<td>b nm</td>
<td>c nm</td>
</tr>
<tr>
<td>Pure ZrO₂</td>
<td>0.5153 ± 0.003</td>
<td>0.5188 ± 0.003</td>
<td>0.5306 ± 0.003</td>
</tr>
<tr>
<td>CZO</td>
<td>0.5114 ± 0.002</td>
<td>-</td>
<td>0.5180 ± 0.002</td>
</tr>
<tr>
<td>YZO</td>
<td>0.5117 ± 0.003</td>
<td>-</td>
<td>0.5158 ± 0.003</td>
</tr>
<tr>
<td>YCZO</td>
<td>0.5103 ± 0.005</td>
<td>-</td>
<td>0.5146 ± 0.005</td>
</tr>
</tbody>
</table>
2.6.4.1 ZO system

Figure 2.13 shows the TGA from room temperature to 950°C of the ZO gel 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. The dehydration of water, occurred around 170°C is represented as

\[
\text{ZrO}_2\text{C}_2\text{O}_4 \cdot 1.5\text{H}_2\text{O} \rightarrow \text{ZrO}_2\text{C}_2\text{O}_4 + 1.5\text{H}_2\text{O}
\]

The oxalate decomposition at 348°C is

\[
\text{ZrO}_2\text{C}_2\text{O}_4 \rightarrow \text{ZrO}_2 + 2\text{CO}_2
\]

There are two more weight losses observed around 480 and 570°C which may be due to the release of chlorine along with the simultaneous crystallization of zirconia.

From the DTA of the dried ZO gel (Figure 2.14), it is seen that there are three peaks in the temperature range 100 to 800°C. The first peak observed around 170°C is due to the dehydration of water as observed in the TGA curve. The second endothermic peak around 350°C is due to the decomposition of oxalate which is also observed in TGA. The amorphous zirconia crystallizes at 441°C in metastable tetragonal (t) phase and the shoulder around 800°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 X-ray pattern (Figure 2.9). Table 2.3 shows the various thermal change processes for the ZO system.
Figure 2.13 TGA curve for the ZO gel powder dried at 40°C.
Figure 2.14: DTA curve for the Z0 gel powder dried at 40°C.
Table 2.3
Thermal analysis data for ZO dried gel powder

<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>14.226</td>
<td>30 - 238</td>
<td>Endothermic</td>
</tr>
<tr>
<td>Organic decomposition</td>
<td>34.640</td>
<td>239 - 460</td>
<td>Endothermic</td>
</tr>
<tr>
<td>Phase formation (or) crystallization</td>
<td>-</td>
<td>414 - 462</td>
<td>Exothermic</td>
</tr>
</tbody>
</table>

2.6.4.2 CZO system

Figure 2.15 shows the TGA of the CZO precursor dried at 40°C. It is found that there are four major weight losses of 16.72%, 15.61%, 15.13% and 3.64%. The first weight loss corresponds to dehydration of water around 170°C and the second weight loss is due to the burning and release of nitrate around 260°C which includes the decomposition of the oxalate also. Indeed, the decomposition of oxalate takes place in two steps. The first step overlaps with the nitrate decomposition and the third weight loss corresponds to the decomposition of the second step of the oxalate which starts at 295°C and ends at 452°C. The observed small splitting in the liberation of nitrate peak in the differential curve of the TGA may be due to the first decomposition step of the oxalate. The final weight loss may be due to the liberation of chlorine around 570°C.

Figure 2.16 shows the DTA of the CZO gel dried at 40°C. It shows one endothermic and three exothermic peaks in the temperature range 30 to 900°C. The endothermic peak corresponds to the dehydration of water and the first exothermic peak observed around 261°C is attributed to the burning and release of nitrates as observed in the TGA. The peak observed around 355°C is due to the decomposition of oxalate which is in agreement
Figure 2.15 TGA curve for the CZO gel powder dried at 40°C.
Figure 2.16 DTA curve for the CZO gel powder dried at 40°C.
with the TGA curve. However, the double step decomposition of oxalate is not resolved in the DTA curve. It is interesting to note that in the pure zirconyl oxalate gel, the decomposition of oxalate is an endothermic process whereas exothermic peak has been observed for the CZO gel. The peak at 463°C corresponds to the crystallization of t phase of zirconia and it remains above this temperature which is clearly observed in the XRD pattern (Figure 2.10). Table 2.4 shows the various thermal change processes for the CZO system.

### Table 2.4

<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>16.718</td>
<td>30 - 200</td>
<td>Endothermic</td>
</tr>
<tr>
<td>Nitrate decomposition</td>
<td>15.614</td>
<td>201 - 300</td>
<td>Exothermic</td>
</tr>
<tr>
<td>Organic decomposition</td>
<td>15.126</td>
<td>301 - 450</td>
<td>Exothermic</td>
</tr>
<tr>
<td>Phase formation (or) Crystallization</td>
<td>-</td>
<td>437 - 487</td>
<td>Exothermic</td>
</tr>
</tbody>
</table>

#### 2.6.4.3 YZO system

Figure 2.17 shows the TGA curve for the YZO dried gel powder in the temperature range 30 to 800°C. It has been observed that there are three major weight losses of 17.91%, 12.22% and 19.74%. The first and second weight losses correspond to the same reason as seen in the previous case. The latter weight loss may be due to the decomposition of oxalate with the simultaneous formation of amorphous tetragonal zirconia powder. Two more weight losses, 1.48% and 2.80% have also been observed. These losses may be due to the liberation of adsorbed/occluded chlorides in the dried gel powder.
Figure 2.17 TGA curve for the YZO gel powder dried at 40°C.
Figure 2.18 shows the DTA curve of the YZO dried gel powder, in which an exothermic and two endothermic peaks have been observed. The endothermic peak around 170°C is due to the dehydration of adsorbed water as observed in the TGA curve. A small endothermic peak around 250°C has been observed which may be due to the removal of structural hydroxyl group and is not resolved even in the DTG curve. The existence and removal of the hydroxyl group has been confirmed by IR spectrum for the samples collected at their peak temperatures, 170°C and 250°C, respectively. The decomposition of nitrate has not been well resolved in the DTA curve. The shoulder around 285°C in the second broad endothermic peak may be due to the decomposition of nitrates which has been clearly identified in the TGA curve. The endothermic peak around 345°C may be attributed to the decomposition of oxalate as observed in the TGA curve. The oxalate decomposition step starts before the complete decomposition of the nitrate. The exothermic peak around 467°C is due to the crystallization of amorphous oxide powder in t phase. This is confirmed by XRD spectrum (Figure 2.11) for the sample which has been isothermally heat treated at 460°C for 1hr. The liberation of chlorides has not been observed in the DTA curve which may be due to the smooth release of the same. Table 2.5 shows the various thermal change processes for the YZO system.

Table 2.5

<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>17.907</td>
<td>30 - 207</td>
<td>Endothermic</td>
</tr>
<tr>
<td>Nitrate decomposition</td>
<td>12.222</td>
<td>207 - 305</td>
<td>Endothermic</td>
</tr>
<tr>
<td>Organic decomposition</td>
<td>19.735</td>
<td>305 - 470</td>
<td>Endothermic</td>
</tr>
<tr>
<td>Phase formation (or)</td>
<td></td>
<td>445 - 508</td>
<td>Exothermic</td>
</tr>
<tr>
<td>Crystallization</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Figure 2.18 DTA curve for the YZO gel powder dried at 40°C.
2.6.4.4 YCZO system

From the TGA curve (Figure 2.19) of the YCZO dried gel powders, it is clear that there are three major weight losses of 18.83%, 17.64% and 12.9%. The first one is due to the dehydration of physisorbed water and the second corresponds to the decomposition of nitrate. The third weight loss may be due to the decomposition of oxalate.

Oxalate decomposition occurs in two steps. The first partial oxalate decomposition overlaps the nitrate decomposition. This is not resolved by the TGA or DTG curves. The second oxalate decomposition occurs in the temperature range from 289 to 462°C. There are two more small weight losses observed in the temperature range from 470 to 640°C. These may be attributed to the smooth release of adsorbed/occluded chloride and residual carbon dioxide respectively.

It can be seen from Figure 2.20, DTA curve for the YCZO dried gel powder, that there is one endothermic and three exothermic peaks corresponding to temperatures around 170, 270, 340 and 470°C respectively which is almost similar to the CZO system. The endothermic peak around 170°C is due to the dehydration of adsorbed water which has been observed in the TGA curve. As observed in the TGA curve, the burning and release of nitrate occur at around 270°C. The peak existing around 340°C, may be attributed to the decomposition of oxalate which has also been observed in the TGA curve. It can be seen that the decomposition of oxalate is not resolved by the DTA curve also. The exothermic peak around 470°C is due to the crystallization of amorphous YCZO powder in t phase with the simultaneous release of chlorides. The formation of t phase has clearly been confirmed by X-ray diffraction patterns (Figure 2.12) for the sample isothermally heat treated at 460°C for 1hr. The liberation of chloride and carbon dioxide has not been observed explicitly in the DTA curve.
Figure 2.19 TGA curve for the YCZO gel powder dried at 40°C.
Figure 2.20 DTA curve for the YCZO gel powder dried at 40°C.
The liberation of chlorine is not observed in the DTA curve, whereas it is observed in the TGA curve around 570°C in the YCZO dried gel powder. The reason is, that the chlorine may be physically adsorbed on the surfaces of the polycrystalline powders. At a temperature above 530°C, the adsorbed chlorine has been released smoothly without any exothermic or endothermic energy release from the surfaces of the particles. Table 2.6 shows the various thermal change processes for the YCZO system.

Table 2.6
Thermal analysis data for YCZO dried gel powder

<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>18.828</td>
<td>30 - 191</td>
<td>Endothermic</td>
</tr>
<tr>
<td>Nitrate decomposition</td>
<td>12.902</td>
<td>191 - 289</td>
<td>Exothermic</td>
</tr>
<tr>
<td>Organic decomposition</td>
<td>17.639</td>
<td>289 - 490</td>
<td>Exothermic</td>
</tr>
<tr>
<td>Phase formation (or) crystallization</td>
<td>-</td>
<td>440 - 506</td>
<td>Exothermic</td>
</tr>
</tbody>
</table>

2.6.4.5 Comparison of thermal studies on ZO, CZO, YZO and YCZO systems

It is quite interesting to note that all the decomposition steps, for the CZO and YCZO dried gel powders, are exothermic in nature (except water dehydration) whereas endothermic peaks have been observed for the ZO and YZO dried gel powders. The observed difference in the decomposition nature of these compounds lies in the presence of cerium ions. During the decomposition process of CZO and YCZO systems, large amount of energy is liberated for the doped gel. Gangadevi et al (1980a; 1980b) have
studied the thermal analysis of zirconyl oxalate dried precipitated powder. The decomposition of oxalate is an exothermic oxidation of carbon mono oxide in air, but in vacuum, the decomposition is endothermic. Based on this suggestion, the release of large amount of energy may be attributed to the exothermic oxidation of carbon mono oxide with carbon dioxide. During the decomposition step, the $\text{Ce}^{3+}$ ions oxidizes to $\text{Ce}^{4+}$ ions. By considering the ionic radius, the possibility of the substitution of the $\text{Ce}^{3+}$ ions in $\text{ZrO}_2$ crystal structure is highly remote at low temperatures and hence the only chance is the formation of $\text{Ce}^{4+}$ ions due to the oxidation of $\text{Ce}^{3+}$ ions. These $\text{Ce}^{4+}$ ions substitute for $\text{Zr}^{4+}$ ions in the $\text{ZrO}_2$ crystal structure and favor the formation of $t$ phase solid solution. There may be a chance for another possibility for the formation of $\text{Ce}_2\text{O}_3$ compound in the oxalate decomposition step. But, the X-ray diffraction patterns (Figures 2.10 to 2.12) do not show the existence of $\text{Ce}_2\text{O}_3$ reflections (Settu and Gobinathan 1994; 1995), which shows authentically, that the observed exothermic peaks are solely due to the exothermic oxidation of YCZO dried gel powder. However, in the reducing atmospheres, at temperatures above 1200°C, the formation of $\text{Ce}_2\text{Zr}_2\text{O}_7$ has been reported (Zhu et al 1992).

In the doped zirconia the crystallization of $t$ phase takes place with different temperatures namely, 463°C for CZO, 467°C for YZO and 470°C for YCZO dried gel powders, whereas the crystallization of metastable $t$ phase is observed at 441°C in pure zirconia. For systems like YZO and YCZO, the formation of small amount of cubic ($c$) phase has also been observed. The X-ray diffraction patterns clearly show these phase formations (Figures 2.9 to 2.12). For all the systems, it is observed from the Tables 2.3 to 2.6, that the crystallization of amorphous powders occurred with simultaneous weight loss.
2.6.5 Powder morphology

Figures 2.21 and 2.22 show the morphology of the ZO, CZO, YZO and YCZO powder samples calcined at 850°C for 1 hour. From the figures, it is clear that the calcined powders of all the samples have irregular shape with varying degrees of agglomeration up to 20μ. These varying degrees of agglomeration may be due to the differences in grinding using the mortar and pestle.

2.6.6 Surface area measurement

Specific surface area has been estimated for the ZO, CZO, YZO and YCZO powders using BET technique with nitrogen. The dried gel powders have been calcined at different temperatures such as 385, 460, 600, and 850°C for 1hr. Assuming the particles are spherical in shape, the average crystallite sizes of the pure and doped zirconia have been calculated by using the formula,

\[ r = \frac{3}{\gamma \rho} \]

Where \( r \) is the average particle size (radius) in nm, \( \gamma \) is the specific surface area in \( \text{m}^2\text{g}^{-1} \) and \( \rho \) is the density of the corresponding calcined powder in \( \text{g}\text{m}^{-3} \). From the Table 2.7, it is found that the surface area of the calcined powders decreases as the calcination temperature increases due to the increase of the crystallite size, which is also reflected in the X-ray diffractograms.

Norman et al (1994) have reported the stabilization of surface area by anions for the pure zirconia system. They have observed that the presence of sulphate ions in the powder resists the decrease of surface area to a certain extent for a wide range of calcination temperatures. In order to
Figure 2.21 SEM pictures for the powders calcined at 850°C for 1 hour. 
a and b are ZO samples; c and d are CZO samples
Figure 2.22 SEM pictures for the powders calcined at 850°C for 1 hour.
a and b are YZO samples; c and d are YCZO samples
Table 2.7
Variation of surface area as a function of temperature measured by BET technique

<table>
<thead>
<tr>
<th>Sample</th>
<th>Firing Tempe. (°C)</th>
<th>Specific Surface Area (m² g⁻¹)</th>
<th>Powder Density g/cc</th>
<th>Average Crystallite Size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZO</td>
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<td>90</td>
<td>2.38</td>
<td>14</td>
</tr>
<tr>
<td></td>
<td>600</td>
<td>20</td>
<td>3.66</td>
<td>41</td>
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<tr>
<td></td>
<td>850</td>
<td>8</td>
<td>3.98</td>
<td>94</td>
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<td>3.10</td>
<td>44</td>
</tr>
<tr>
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<td>11</td>
<td>3.79</td>
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<tr>
<td></td>
<td>850</td>
<td>4</td>
<td>4.72</td>
<td>159</td>
</tr>
<tr>
<td>YZO</td>
<td>460</td>
<td>34</td>
<td>3.68</td>
<td>24</td>
</tr>
<tr>
<td></td>
<td>600</td>
<td>23</td>
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<td>5.3</td>
<td>5.05</td>
<td>112</td>
</tr>
<tr>
<td>YCZO</td>
<td>460</td>
<td>35</td>
<td>3.73</td>
<td>23</td>
</tr>
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<td>27</td>
<td>4.12</td>
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<tr>
<td></td>
<td>850</td>
<td>6</td>
<td>4.39</td>
<td>114</td>
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</table>
increase the surface area of zirconia, dopants are added with the pure zirconia followed by conventional heat treatment (MEL Cat. No. 1010). In contrast to this, the present study shows that there is no increase in the surface area for the doped zirconia.

2.6.7 IR Characterization

Figures 2.23a to 2.23d show the IR spectrum for ZO, CZO, YZO and YCZO powders dried at 40°C. It has been reported that the oxalate ion has quadridentate structure with zirconium ion (Etienne et al 1990). It seems that the addition of yttrium and cerium ions as salts of nitrates do not affect the structure of the zirconyl oxalate. The appearance of the peak at 1390 cm⁻¹ is due to the presence of nitrates in the dried and doped oxalate gel powders. On calcination of the dried gel powders, dehydration of water, decomposition of nitrate and oxalate are observed, similar to the TGA and DTA results. As mentioned earlier the small peak around 250°C in the DTA, result of the YZO dried gel powder, is due to the removal of the hydroxyl group which was confirmed from the spectrum taken for the sample collected at this peak temperature. Table 2.8 shows the vibrational frequencies of the dried powders of the ZO, CZO, YZO and YCZO gels.

2.7 CONCLUSION

Transparent, physical and thixotropic ZO, CZO, YZO and YCZO gels have been prepared by oxalate gelation from metal salts of chlorides, nitrates and oxalic acid in triple distilled water.

Possible reasons for the various stages of the formation of the gels, by means of DLVO theory, have been explained. With the aid of the repeptizable character it is possible to prepare concentrated sols which may be useful for industrial purposes.
TGA studies show that the weight loss is up to 53% for almost all samples. DTA studies show the CZO, YZO and YCZO dried amorphous gel powders are crystallized in t phase whereas, the ZO dried amorphous gel powder is crystallized in metastable t phase, which subsequently transforms to a m phase of zirconia.

The thermal behavior of ceria containing samples is quite different from the others. The oxidation of cerus ions is observed in these samples.

The crystallization of different phases has been confirmed by the powder X-ray diffraction studies. SEM pictures show the agglomerated nature of the calcined powders. This nature has been confirmed from the surface area determinations.

IR studies show the formation of quadridentate structure of the oxalate ions with zirconium ions. The addition of dopants has not altered the structure of the zirconyl oxalate.

These amorphous dried gel powders may be useful for the preparation of the fine m and t phase zirconia polycrystalline powders.
Figure 2.23 IR spectrum for gel powders dried at 40°C
a. zo, b. czo, c. yzo and d. yczo
## Table 2.8
Assignment of the IR bands

<table>
<thead>
<tr>
<th>Vibrational frequencies (cm⁻¹)</th>
<th>Etienne et al (1990)</th>
<th>ZO</th>
<th>CZO</th>
<th>YZO</th>
<th>YCZO</th>
<th>Group</th>
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<tbody>
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<td>1680</td>
<td>1680</td>
<td>1680</td>
<td>1670</td>
<td>1670</td>
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<td>$v_{as}(C=O)$</td>
</tr>
<tr>
<td>1427</td>
<td>1425</td>
<td>1425</td>
<td>1420</td>
<td>1420</td>
<td></td>
<td>$v_{s}(C-O) + v(C-C)$</td>
</tr>
<tr>
<td></td>
<td>--</td>
<td>1390</td>
<td>1380</td>
<td>1385</td>
<td></td>
<td>$(NO_3)^-$</td>
</tr>
<tr>
<td>1356</td>
<td>1350</td>
<td>1355</td>
<td>1350</td>
<td>1355</td>
<td></td>
<td>$v_{s}(C-O) + \delta(O-C=O)$</td>
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<tr>
<td>899</td>
<td>898</td>
<td>900</td>
<td>880</td>
<td>885</td>
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<td>$v_{s}(C-O) + \delta(O-C=O)$</td>
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<td>810</td>
<td>815</td>
<td>805</td>
<td>805</td>
<td></td>
<td>$v_{s}(Zr-O) + \delta(O-C=O)$</td>
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<tr>
<td>470</td>
<td>470</td>
<td>480</td>
<td>470</td>
<td>475</td>
<td></td>
<td>$(Zr-O-Zr)$</td>
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