CHAPTER 2
SYNTHESIS METHODS

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Highlights

Synthesis process
Sol-gel method
Fuel

Abstract

The present chapter focuses on the synthesis methods used in the preparation of nanoparticles. The brief discussion of ceramic method, co-precipitation, combustion synthesis, micro-emulsion, hydrothermal is made in this chapter to have an idea about the various synthesis procedures.

The detail of sol-gel method with flowchart is given for better understanding of the method. The various fuels that can be used in the synthesis of spinel ferrite nanoparticles were discussed.
2.1: INTRODUCTION

The synthesis of a material is an important criterion for the good quality and desired applications. Knowledge of the various experimental methods available for the synthesis of solid therefore becomes an important and integral part of solid state chemistry. Tailor making materials of the desired structures and properties is the main goal of materials science and solid state chemistry.

Rational synthesis of materials requires knowledge of crystal chemistry besides, thermodynamics, and phase equilibrium and reaction kinetics. An understanding of the crystal chemistry is of essence in designing new materials possessing desired properties.

The synthesis of solids can be achieved by number of methods. These methods are grouped into ceramic and wet-chemical methods. The traditional ceramic method involves mixing and grinding of the constituent oxides, carbonates and heating them at high temperature with intermediate grinding when necessary. A wide range of conditions such as high temperature and pressure, very low oxygen fugacity’s and rapid quenching have all been employed in the synthesis of materials. Low temperature chemical routes and such methods involving mild reaction conditions are of great interest.

The soft chemistry route are desirable because they lead to novel products, many of which are meta-stable cannot otherwise be prepared. Soft chemistry routes essentially makes use of simple
reactions such as inter calation, ion exchange, hydrolysis, dehydration and reduction that can be carried out at sufficiently low temperature.

In the recent years synthesis of nano-crystalline materials has gained lot of importance. The synthesis route for nano-crystalline materials are classified in two ways; one way is based on the starting state of the material namely gas, liquid and solid. The methods like vapor condensation like chemical vapor deposition etc. use the gaseous state of the matter whereas methods like sol-gel, chemical and electrochemical deposition etc. used liquid as starting materials. The methods like high energy ball milling, nano lithography etc. start with solids for synthesizing nano-crystalline materials.

However, the synthesis routes are also classified as top down approach and bottom of approach. In the bottom up approach individual atoms and molecules are brought together or self assembled to form nano-structured materials in at least one dimensional material. The techniques that start with liquid and gas as their starting materials fall in this category. The bottom up techniques can give very fine nanostructures of individual nano-particles, etc., with narrow size distribution. The top down techniques do not lead to nano-particles, however they can produce bulk nano-structured materials. The bottom up approaches has difficulties in scale up, while the top down approaches can be easily scaled up.

Preparation of new solids need not necessarily involved a new method. Synthesis of new solid is not always achieved by design. The
synthesis of spinel ferrites by various methods have been discussed in this chapter.

2.2: CHEMICAL REACTIONS

Various types of chemical reactions have been used for the synthesis of the solid materials. Some of the common reactions employed in the synthesis of inorganic solids are

1. Decomposition
   \[ A (s) \rightarrow B (s) + C (g) \]
   \[ A (g) \rightarrow B (s) + C (g) \]

2. Addition
   \[ A (s) + B (g) \rightarrow C (s) \]
   \[ A (s) + B (s) \rightarrow C (s) \]
   \[ A (s) + B (1) \rightarrow C (s) \]
   \[ A (g) + B (g) \rightarrow C (s) \]

3. Metathetic reaction (which combines 1 and 2 above)
   \[ A (s) + B (g) \rightarrow C (s) + D (g) \]

4. Other exchange reactions
   \[ AX (s) + BY (s) \rightarrow AY (s) + BX (s) \]
   \[ AX (s) + BY (g) \rightarrow AY (s) + BX (g) \]
   \[ AX (s) + AY (s) \rightarrow AY (s) + BX (s) \]

Typical examples of the above reactions are mention below;

1. \[ CaCO_3 (s) \rightarrow CaO (s) CO_2 (g) \]
2. \[ YBa_2 Cu_3O_6 (g) \rightarrow YBa_2 Cu_3O_6 \_7 (s) \]
3. \[ CO(g) + MnO_2 (s) \rightarrow CO_2 (g) + MnO (s) \]
4. \[ ZnS (S) + CdO (s) \rightarrow CdS (S) + ZnO(s) \]

Some of the methods used for the synthesis of a material are discussed in brief [1, 2]
2.3: CERAMIC PROCESS

The most common method of preparing inorganic solids is by the reaction of the component materials at elevated temperature. If the components are solids the method is called ceramic method. Ceramic process is the most commonly used method for the preparation of metal oxides and solid materials. The method involves grinding powders of carbonates, oxalates, oxides or other compounds containing the relevant metals. The grinding takes place for about three to four hours. The ground mixture is then heated at about 1000 °C or more than that to produce homogeneous mixture. In some cases the grinding and heating is carried out at two stages (double sintering). The sintered powder is pelletized using hydraulic press by applying some suitable pressure. Knowledge of phase diagram is essential in order to fix the desired composition and condition for synthesis. The knowledge of container is also important. Platinum, silica, alumina, crucibles are used for the synthesis of metal oxides, while graphite containers are generally used for the synthesis of sulphides and other chalcogenides. Tungsten and tantalum containers are quit inert to the metals and halides and have been used in many preparations, especially of halides. If one of the constituent is volatile or sensitive to the atmosphere, the reaction is carried out in sealed evacuated capsules. Most ceramic preparation requires high
temperature and therefore the reaction is carried out in muffle furnace. In some of the preparation oxygen/nitrogen gas is passed.

2.4: CO-PRECIPITATION

In co-precipitation method, the required metal cations are soluble slats like nitrates (NO₃), chlorides (Cl₂) or sulphates (SO₂) are co-precipitate from a common media, usually as hydroxides or citrates the precipitate after drying is heated to the required temperature in a desired atmosphere to get the final product. Homogeneous precipitation can yield crystalline amorphous products.

2.5: COMBUSTION SYNTHESIS

Combustion synthesis or the self propagating high temperature synthesis is a versatile method for the synthesis of variety of solids. In this method, use of highly exothermic reaction between the reactants to produce a flame due to spontaneous combustion is carried out which then yields the desired products or its precursor in fine lose powder. In order to combustion to occur one has to ensure that the initial mixture of reactant is highly dispersed and contains high chemical energy.

In order to carry out the combustion synthesis, the powdered mixture of the reactants is generally placed in air or oxygen medium that provides an exothermic reaction on ignition. The combustion temperature can be anywhere between 1500 and 3500 K depending on the reaction. The reaction time is very short because the desired products results soon after the combustion.
2.5: MICRO-EMULSION METHOD

Micro-emulsion synthesis is one of the attractive, easy and cheaper methods for the preparation of ferrite nano-particles. It produced fine particles of nanosize dimension with chemical homogeneity. The method has been used to synthesize several ceramic systems of technologically important. The method is based on the use of nanosize domains in a micro-emulsion as the micro-reactors to regulate the dimension of precursor. An inverse micro-emulsion is regarded as thermodynamically stable isotropic dispersion of an aqueous phase in the continuous oil phase, stabilized by an interfacial layer of surface active molecules. The dynamic nature of micro-emulsion, reactants from two micro-emulsions will come in contact with each other when they are mixed together, as a result of collision and coalescence of the droplets. Therefore, a precursor will be formed in the aqueous domain if the reaction involves a precipitation or co-precipitation. The reaction may also be carried out by adding one reactant in the form of a liquid or a gaseous phase into a micro-emulsion containing the other reactant.

2.6: HYDROTHERMAL METHOD

Hydrothermal method is also a solution phase root to synthesis of nano-particles. In this method, the reactants are mixed in an aqueous phase and placed within a sealed reaction vessels which is then heated to temperatures varying between 100-300 °C [3,4]. Since the volume is
constant, the increased pressure induces a state in which water exists as a liquid at a temperature higher than its normal boiling point. These conditions lower the viscosity of the solvent leading to increase in reaction kinetics by increasing the solubility and mobility of the dissolved species (metal cations). In turns the particle formation occurs faster than it would at a lower temperature, thereby increasing particle uniformity.

Hydrothermal method of synthesis of metal oxides is generally done through hydrolysis of metal salts. The phase purity can be influenced by the initial reactants and by varying the pH. The method has some drawbacks includes formation of other phases at higher temperature, lack of control over the particle size and size distribution etc.

2.7: SOL-GEL SYNTHESIS

The sol-gel method is one of the important technique of preparing inorganic solids. It is a wet-chemical method and involves several process (chemical and physical). The name sol-gel is given to the process because of the distinctive viscosity increase that occurs at a particular point in the sequence of steps. A sudden increase in viscosity is a common feather in sol-gel processing indicating the onset of gel formation.

The method has several advantages over the conventional ceramic method. Better homogeneity, high purity, lower synthesis temperature, more uniform phase distribution in multi-component
system, easy preparation, cost effective etc. are the advantages parameters [5-7].

The sol-gel method is a multi-step method; some of the steps are discussed below;

1. **Hydrolysis**
   
The process of hydrolysis may start with a mixture of metal oxide as water in a solvent at the ambient or a slightly elevated temperature. Acid or base catalyst are added to speed up the reaction.

2. **Polymerization**
   
This step involves condensation of adjacent molecules wherein H$_2$O and alcohol are eliminated and metal oxide linkages are formed. Polymetric network group to colloidal nitrate group in the liquid state/sol state.

3. **Gelation**
   
In this step he polymeric network linkup to form a three dimensional network throughout the liquid. The system becomes somewhat rigid which is a characteristic of a gel, on removing the solvent from the sol. Solvent as well as water and alcohol molecules, however, remain inside the pores of the gel. Aggregation of smaller polymeric units to the main network progressively continues on aging the gel.

4. **Drying**
   
Here, water and alcohols are removed at moderate temperature (<470 K), leaving a hydroxylated metal oxide with residual organic content. If
the objective is to prepare a high surface area aero gel powder of low bulk density, the solvent is removed super critically.

Figure 2.1: Flow chart of sol-gel auto-combustion technique

5. Dehydration

This steps is carried out between 670 and 1070 K to drive off the organic residues and chemically bound water, yielding a glassy metal oxide with up to 20-30% micro-porosity.

6. Densification

Temperatures in excess of 1270 K are used to form the dense oxide product.

The flow chart of the sol-gel method is given above;
2.8: FUELS/CHELATING AGENT

In the synthesis of magnetic nano-particles of spinel ferrite using sol-gel auto combustion method, various fuels/chelating agent were commonly used with different ratio of metal nitrates to fuel. The commonly used fuels are citric acid [8], glycine [9] and Cellulose [10]. In addition to this, L-ascorbic acid, tartaric acid, Succinic acid can also be used as a fuel in the sol-gel method. Some of the physical properties, chemical formula, structural formula etc of the fuels used in the present work are discussed in the following lines.

In the sol-gel synthesis process, the synthesis parameters like pH, fuel, annealing temperature etc. plays a crucial role in governing the properties of materials.

Role of pH

pH is the measure of the activity of the hydrogen ion, which measures a hydrogen ion concentration, is closely related to and is often written as pH. Solutions with a pH less than 7 are said to be acidic and solutions with pH greater than 7 are basic or alkaline. The pH of the solution is one of the main factor on which final composition of the product depends which can be varied to get desired final product. The pH of the solution can be varied from 7 to 12 by adding aqueous ammonia solution. Increasing pH values contributes to crystallinity of the product material. In the literature the studies related to the effect of pH on the properties of spinel ferrite are reported [11]
**Role of fuel/chelating agent**

The sol-gel auto-combustion method requires fuel/chelating agent for ignition of the reaction. Citric acid, glycine, dextrose, tartaric acid, oxalic acid, glucose etc. were used as a fuel in the synthesis procedure. Among these fuels, citric acid is used commonly as a fuel.

The fuel nature is affecting the auto-combustion reaction intensity and the duration of thermal treatment which implies specific structural characteristics and magnetic property. Table 2.1 gives the list of fuels used in the synthesis of spinel ferrite nano-particles using sol-gel auto-combustion method [12]

**Role of annealing temperature**

The sol-gel auto-combustion method yields a fine powder of nanosize nature. The as-prepared powder may show amorphous nature and therefore it requires annealing. Usually, for spinel ferrites the annealing temperature is around 500-600°C and annealing time ranges from 4-12 h. for good crystallization of the obtained powder annealing is necessary. It is reported that as annealing temperature increases the crystallite size and thereby changes the structural, electrical, dielectric and magnetic properties of spinel ferrites [13].
Table 2.1: Structural, molecular weight, total valence and decomposition temperature of the fuels

<table>
<thead>
<tr>
<th>Chelating Agent</th>
<th>Structural formula</th>
<th>Mol. Wt. (g/mol)</th>
<th>Decomposition temp.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Citric acid</td>
<td><img src="" alt="Citric acid" /></td>
<td>210.14</td>
<td>153 °C</td>
</tr>
<tr>
<td>Urea</td>
<td><img src="" alt="Urea" /></td>
<td>60.06</td>
<td>135°C</td>
</tr>
<tr>
<td>Glycine</td>
<td><img src="" alt="Glycine" /></td>
<td>75.07</td>
<td>262°C</td>
</tr>
<tr>
<td>Hydrazine</td>
<td><img src="" alt="Hydrazine" /></td>
<td>32.05</td>
<td>250°C</td>
</tr>
<tr>
<td>Tartaric acid</td>
<td><img src="" alt="Tartaric acid" /></td>
<td>150.087</td>
<td>171–174 °C</td>
</tr>
<tr>
<td>Dextrose</td>
<td><img src="" alt="Dextrose" /></td>
<td>180.16</td>
<td>146 °C</td>
</tr>
<tr>
<td>Succinic acid</td>
<td><img src="" alt="Succinic acid" /></td>
<td>118.09</td>
<td>184 °C</td>
</tr>
<tr>
<td>L-ascorbic acid</td>
<td><img src="" alt="L-ascorbic acid" /></td>
<td>176.12</td>
<td>190-192 °C</td>
</tr>
</tbody>
</table>
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