Sol-gel Synthesis of Co^{2+} Substituted Zn-Cr Oxide Nanoparticles

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Abstract:

Metal oxide nanoparticles of Co^{2+} substituted zinc – chromium were synthesized by using sol-gel self ignition method by using the metal nitrates of constituent elements. The starting materials are mixed together according to their weight percentage in the composition. The synthesis approach and synthesis conditions highly affect the structure of composition and its physical and

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chemical properties. In the present chapter we discuss the bottom – up approach for the synthesis of metal oxide nanoparticles at low temperature. The stages involved in the preparation of metal oxides via sol-gel route. The silent features and applications of metal oxide nanoparticles are also discussed.

Key words: Cobalt oxide, bottom-up approach, sol-gel auto-combustion,

1. Introduction:

Because of the wide range of applications for catalysts, sensors, microelectronic devices to energy conservation devices which includes solar and fuel cells and spintronic devices [1-6], metal oxides and their alloys attract much more interest of materials scientists and engineers. The physical and chemical properties show revolutionary modification in smaller scale and its application in various fields. Nano sized alloys of metal oxides synthesized by chemical route to provide a convenient process for the preparations of nanostructure ceramic powder at comparatively low cost, low temperature, less time. In this chapter the details of synthesis methods used to prepare the cobalt substituted Zn-Cr oxide nanoparticles.

2. Composition of Metal Alloys:

Metal nitrates of selected metals are used as starting materials for the preparation of metal oxides. They are easily available, low cost and high purity. The selected ferrites preparation to keeping its valence (charge balancing) and comparable radii carefully selected for making samples. Following series is prepared by using sol-gel auto combustion technique, CoxZn0.95-xCr0.05O (x = 0.0, 0.02, 0.04, 0.06, 0.08 and 0.1)

3. Synthesis Methods:

Numbers of physical and chemical synthesis methods for the preparation of metal alloys are available for the preparation of ferrite materials. For the most practical applications, the materials with single phase structure are very essential. High quality single phase structured materials requires careful attention of various parameters such as purity of row materials, chemical composition, nature and type of dopant, sintering time and temperature, sintering atmosphere, sintering rate, gain size etc. Solid state reaction method is generally employed for the preparation of metal oxides in order to achieve the above requirements. Material synthesis plays an important role in developing the new materials with different properties. Ceramic method [7], Electrochemical method [8], Hydrothermal method [9], chemical – co-precipitation method [10], sol-gel auto-combustion method [11], microemulsion method [12], microwave – refluxing [13] are some of the most frequently used synthesis methods for the preparation of metal oxides.

3.1 Sol-Gel Synthesis Method:

Over the last few years, the sol-gel technique attracts scientists for the preparation of mixed metal oxides in the nanoparticles range at relatively low temperature and cost [14]. This method belongs to wet chemical method which consist both chemical and physical processes during the synthesis of nanoparticles. In this method at a particular step, the viscosity of the mixture suddenly increases which is a common

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feature of sol-gel process indicating the beginning of gel formation [15-16]. It has been demonstrated that the sol-gel process has remarkable advantages over traditional methods such as better mixing and the chemical homogeneity. The main features of the sol-gel auto-combustion technique are as bellow,

- The materials obtained by using sol-gel method have better homogeneity
- The sol-el synthesized powders are obtained with no/negligible amount of impurity addition.
- As compared to other synthesis methods, this method requires low sintering temperatures.
- This method provides better size and morphological control to the compounds.
- Most significant phase distribution in multi-element systems like ferrites.
- The samples prepared via this route require low cost.

a) *Hydrolysis:* The process of hydrolysis started with a mixture of metal nitrates and water with a chelating agent usually citric acid at the ambient or slightly elevated temperature.

b) *Polymerization:* In this step condensation of adjacent molecules will be formed and H2O and NO3 molecules are eliminated with the formation of metal oxide linkages. Polymeric networks grow to colloidal dimensions in the sol (liquid) state.

c) *Gelation:* In gelation, the polymeric networks are linked up and form a three dimensional network inside the whole liquid. In the

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process of removing the solvent from the sol, the mixture becomes somewhat rigid. Solvent as well as water and NO3 molecules remain present inside the pores of the gel.

d) *Drying:* By applying the moderate temperature H2O and NO3 molecules are removed leaving a hydroxylated metal oxide.

e) *Dehydration:* This is a very important step which is carried out in a temperature range of 450 to 850 °C. In this process all the impurities and chemically bounded water is removed from the powders which yields the pure composition of metal oxide.

f) *Densification:* Above 1000 °C, the temperatures are used to obtain the oxides in the form the dense products.

3.2 Advantages of Sol-gel Method:

Since the sol-gel method belongs to the chemical methods of preparation, it has many advantages over other methods of preparation. This method provides homogeneous mixing of constituents at molecule level and has good stoichiometric control. This method involves an aqueous-based processing system at low-processing temperature which produces the active powders. The details of these advantages are described below.

1. The intimate mixing of the elements in gel form results in reaching the ingredients in a very short interval of time to form the material considerably at lower temperatures than in conventional solid state processing, often by several hundred degrees. This makes it possible to obtain low temperature modifications of

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meta-stable phases thereby controlling the stoichiometry of ceramics containing volatile oxides.

2. Sol-gel method does not require any grinding procedure to achieve homogeneous single phase ceramics, thereby avoiding a potential source of contamination. The purity of precursors makes the sol-gel process an excellent method for making high purity materials. Grinding of powders also produce dust, which is hazardous and can be avoided.

3. The wet processing is a highly controllable method for the preparation of small sub-micron oxides. The precise size control of the particles is also strength of sol-gel processing. The particles can be used e.g. as porous beads, as filters, or as starting materials for polycrystalline compounds. In the preparation of ceramic bodies, a controlled particle size distribution can yield very high green densities, which might be sintered into fully dense bodies. Controlled particle size gives a material with better densification.

4. Conventional ceramic processing cannot yield high surface areas and small pore sizes that are typical for inorganic gels. The possibility of controlling the porosity is highly attractive especially for applications such as catalysis, thermal or acoustical insulations, filtration, separation and chromatography.

The sol – gel method has most successful use in coatings and films. Compared to other common film preparation techniques such as chemical vapor deposition (CVD), atomic layer deposition (ALD) and physical vapor deposition (PVD), the equipment needed for sol-gel film deposition is relatively simple and inexpensive. Another possibility is to coat the surface with complex shapes, such as tubes and fibers. In these materials, coating makes the phase distribution more homogeneous compared to mixed powders and it also inhibits the grain growth during sintering, thereby proving a way to tailor made properties of the composite.

4. Sample Synthesis via Sol-Gel Route:

The methods such as wet-chemical co-precipitation and hydrothermal produces fine powders with very small sized particles but they have some disadvantages such as long synthesis time, washing and drying process, and loss of metal ions reduce their suitability for large scale production [20]. In the recent year's sol-gel auto-combustion method have been used extensively due to its low temperature and less time synthesis advantages. In the present work we prepare the Ni0.5Co0.5FeAlO4 ferrite nanoparticles by using sol-gel auto-combustion technique.

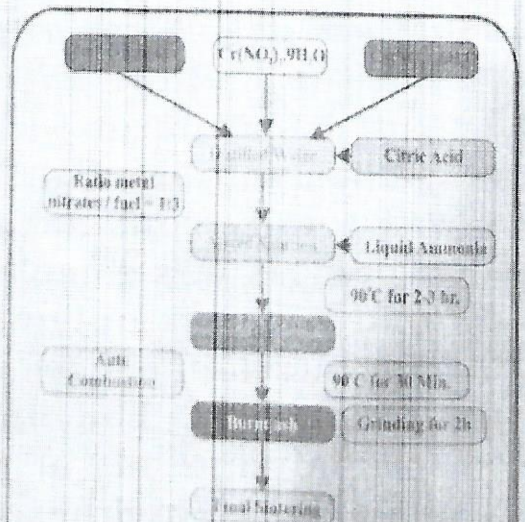

Figure 1: Flow chart of CoxZn0xZn0.95-xCr0.05O **Nanoparticle Synthesis**

Cobalt nitrate ($Co(NO_3)_2 \cdot 3H_2O$), Zinc nitrate ($Zn(NO_3)_3 \cdot 9H_2O$), and Chromium nitrate ($Cr(NO_3)_3 \cdot 9H_2O$), citric acid ($C_6H_8O_7 \cdot H_2O$) with high purity (99% pure) were used as initial materials for the synthesis of $Co_xZn_{0.95-x}Cr_{0.05}O$ oxide nanoparticles via sol-gel route. Whole reaction was carried out in air atmosphere without protection of inert gases. All metal nitrates were mixed thoroughly in double distilled water and citric acid was mixed in the solution by taking the molar ratio of citric acid with metal nitrates as 1:3 with their weight proportion. The whole mixture is kept on magnetic stirrer with hot plate. To maintain the pH = 7 of the solution, liquid ammonia was poured slowly with continuous stirring the mixture until the pH maintains at 7. Along with continuous stirring, the mixture is then heated at constant temperature of 90°C. Due to heat treatment evaporations process starts and after some time the mixed solution was converted into viscous sol and finally converted in to viscous brown gel. After removal of water content from the mixture the dark brown gel was self ignited and burnt with glowing flints. In the decomposition process the entire citrate complex was totally consumed and the auto-combustion process was completed. Finally, the brown colored ash was obtained as a yield of the auto-combustion process which can be called as 'precursor'. The final powder was subjected to final sintering at 600°C for 6 hrs. The flow chart of the synthesis of $Co_xZn_{0.95-x}Cr_{0.05}O$ oxide nanoparticles by using sol-gel method is shown in figure 1.

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