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A comparative study on synthesis techniques of Nanoferrites and its applications

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Abstract—Nano-materials are the particles with the both external and internal structural dimensions declining in the range of 1–100nm. Nanomaterials exhibit unique optical, electrical, mechanical, and quantum properties at this scale in contrast to their molecular-scale behavior. In a thorough introduction, the current review describes the methods of synthesis and uses of nanoferrites in a variety of electrical and electronic applications, magnetic recording applications for audio and videotapes, high density digital recording discs, computer memory, antenna fabrication etc and in medical field for cancer treatment and in MRI, in household appliances. The benefits of the Co-Precipitation approach over hydrothermal and sol-gel synthesis procedures for the creation of nanoferrites were the main focus of this review.

Keywords—Nano ferrites, Hydro thermal method, sol-gel method, Co-precipitation method, Environmental applications.

I. INTRODUCTION

A class of magnetic oxide compounds with iron oxide as its main constituent are usually referred to as "ferrite." The first magnetic substance known to the ancient people was magnetite (Fe_3O_4), commonly known as loadstone. It is a true ferrite [1]. In modern catalytic organic synthesis, the spinal ferrite nanoparticles are an efficient and important tool in the early 21st century because of their remarkable magnetic and electronic characteristics (separated easily by an external magnet), but as compared to the characteristics of the conventional bulk materials, there are quite different[2]. Due to their exceptional physical and chemical characteristics, spinel ferrite nanoparticles, a type of soft magnetic material, have become a prominent area of research in nanotechnology, nanoscience, and nano electronics. On the basis of crystal structure Spinel ferrites, magnetic materials with nanoscale dimensions, have a variety of intriguing applications. They are magnetically soft due to their high electrical resistivity and low magnetic loss. Because of their exceptional magnetic properties, spinel ferrites are employed as an alternative to metallic magnets like Fe and layered Fe-Si alloys [3].Spinel ferrites are nanosized, and their chemical formula is MFe_2O_4.M refers to the divalent metal ions, which include Mg, Mn, Co, Zn, Cu, Ni, and Cd and Other trivalent ions, such as Al^{3+}, Cr^{3+}, Ga^{3+}, etc., can take the place of Fe^{3+}e.t.c.Spinel ferrite with nanoscale dimensions typically has the formula AB_2O_4, which crystallizes in a cubic structure. A unit cell of the spinel lattice is made up of 32 oxygen anions. These anions are arranged in a face-cantered cubic pattern, leaving two different types of spaces between them: tetrahedral or A-site, which is surrounded by four oxygen ions, and octahedral or B-site, which is surrounded by six oxygen ions [4].The cation distribution for tetrahedral and octahedral sites Spinel ferrites are classified as normal, inverse, and random spinel ferrite. The difference between spinal and inverse spinal structure is that, in spinal structure $((A^{II})^{tet}(B^{III})^{oct}O_4))$,B ions occupy 1/2th of the octahedral sites while A ions occupy 1/8th of the tetrahedral sites[5] where as in inverse spinal structure $((B^{III})^{tet}(A^{II})^{oct}(B^{III})^{oct}O_4))$, all A cations and half of the B cations occupy octahedral sites and other half of B cations occupy tetrahedral sites[6]. For example in spinal structure, zinc ferrite ($ZnFe_2O_4$) and cadmium ferrite ($CdFe_2O_4$), which has the divalent metallic ions Cd^{2+} or Zn^{2+} at the (A) sites and the ions of Fe^{3+} at the (B) sites[7]. Similarly nickel ($NiFe_2O_4$) and cobalt ferrites ($CoFe_2O_4$) has an Inverse spinel structure with Fe^{3+} ions easily distributed between the A and B sites, Co^{2+} or Ni^{2+} ions almost evenly distributed between tetrahedral (A) and octahedral (B) sites, and Co^{2+} or Ni^{2+} ions primarily put in octahedral (B) locations [8].

The chemical and mechanical stabilities of spinel and inverse spinal nano ferrites are very different from their bulk counterparts. Due to all of these properties, nano ferrites have been broadly utilized in biotechnology, catalysis, biomedical, magnetic drug delivery, solar cells, magnetic cards, recording devices, and sensors [8-10].Below a specific temperature, referred to as the Curie temperature(T_c), the nano ferrite compounds show good magnetic characteristics. Fundamental and applied studies have concentrated on the synthesis and analysis of nano-sized ferrite particles with an emphasis on their size-dependent characteristics. The basic structural characterisation approaches do not provide information on the degree of ion dispersion in the tetrahedral and octahedral sites.

II. FERRITES PREPARATION METHODS

Ferrite nanoparticles can be synthesized chemically in a variety of ways, including hydrothermal, chemical vapour deposition, sol-gel, co-precipitation, and other techniques. In In this context, we've talked about how nano ferrites are made using the Sol-Gel, hydrothermal, and co-precipitation methods.[11].

Hydrothermal Method

A different number of preparation methods, for instance, hydrothermal synthesis have been used and explored for producing ferrites nanoparticles. But the ferrite nanoparticles which are produced Out of all the preparation methods, the easy one is hydrothermal technique, as they are cheap and versatile too. Two factors are significant in the hydrothermal process. One is the hydrothermal synthetic method’s optimization, and the other is ferrite nanoparticles surface modification or ion doping. Ion doping can cause many effects which include cation redistribution, changes in lattice strain and size of the grain, structure disorder, and effects in chemical and physical characteristics of the ferrite nanoparticles. Controlling the size and surface area of the materials is largely accomplished through the use of synthesis processes. The synthesis of nanoparticles of magnetic materials (ferrites) have been reported using, hydrothermal technique. By changing the temperature, pH value, and alkoxide concentration with the addition of water and alcohol, hydrolysis is carried out. The temperature variation of this method is 100–400^{0}C.The hydrothermal process is a low-cost, low-temperature method that enables accurate control of the chemical composition of the final product [12]. Hydrothermal process was employed to synthesize a wide range of ferrites; i.e., both hard and soft ferrites.

For producing ferrite nanoparticles on a large scale, the hydrothermal approach is highly effective. In general, this process has a very high yield of nanoparticles. $M(NO_3)_2{\bullet}6H_2O$,$Fe(NO_3)_3{\bullet}9H_2O$, and NaOH are used as precursors in the synthesis of MFe_2O_4 nanoparticles (M = Ni, Co, Mn, and Zn). A solvent is deionized water [13]. By keeping the nitrates (g) to water (ml) ratio at 1:3, metal and iron nitrates can dissolve in distilled water. The resulting mixture is continuously stirred until nanoparticles form. The ratio of NaOH to nitrates is added to the mixture at a rate of 1:4. To produce pure spinal phases, the mixture's pH is kept at 11.In addition, the mixture is put into a 300 ml Teflon-lined steel autoclave after being aggressively agitated for two hours. Heat treatment for the sealed autoclave lasts 48 hours at 150^{0}C. The autoclave is gradually cooled to room temperature after 48 hours (RT). Once the autoclave's pH level hits 7, it is filtered and cleaned with acetone and distilled water. The resulting ferrite nanoparticles are then removed and dried for six hours at 60^{0}C. [14,15].Figure.1 shows how the synthesis part is represented.

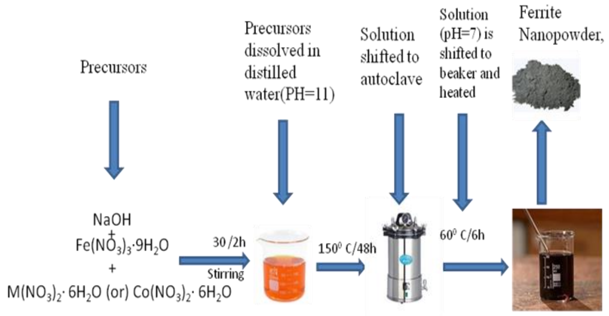

Figure 1. Synthesis technique for nano ferrites via hydro thermal method.

This technique has some advantages, including producing high-quality 1D nanostructures at a low cost and in a simple and easy way. The disadvantages of this method are, it has long reaction time, utilization of highly concentrated NaOH solution, slow reaction of kinetics at any given temperature and the requirement of a high-pressure reactor which limits the large scale production of materials[16].

Sol–gel Auto Combustion Method

The ferrite nanoparticles prepared by using auto combustion sol–gel method by taking high purity nitrates of the constituent ions and L-ascorbic acid (L-ascorbic Acid is a natural water soluble vitamin-C its Molecular formula is $C_6H_8O_6$)as a fuel. Sol–gel auto-combustion synthesis method is an easy and convenient method for obtaining nanoparticles of spinel ferrite. Sol–gel technique offers enhanced control over homogeneity, elemental composition and powder morphology. The technique of preparation, experimental settings, and other parameters have a significant impact on the physical and chemical characteristics of spinel ferrite nanoparticles[17]. It is required to obtain materials with controlled stoichiometry and small, homogeneous grains in order to produce materials with the correct characteristics for various applications. This can be accomplished by using the sol-gel auto-combustion synthesis method. Figure .2 shows the flow chart for the synthesis of nanoferrites using this method.

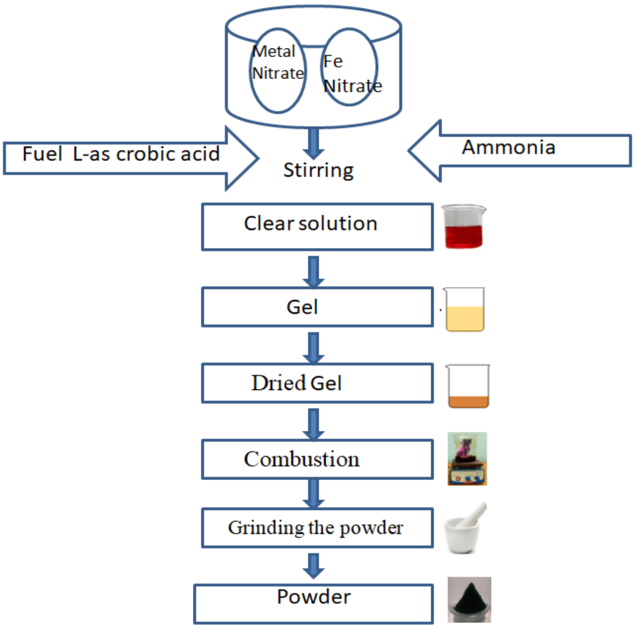

Figure 2. shows the process flow for making ferrite nanoparticles using the sol-gel approach.

The metal nitrates (M = Ni, Co, Mn, and Zn) of the suitable ions and L-ascorbic acid were used as fuel in the well-known sol-gel auto combustion technique to produce the ferrite nano-powders. Amounts of $M(NO_3)_2$,$Fe(NO_3)_3$ with molar ratio $M^{2+/}Fe^{3+}$=1/2 were dissolved completely in de-ionized water. The aqueous solution containing M^{2+} and Fe^{3+} ions was added to L-ascorbic acid (it is a natural water –soluble vitamin its Molecular formula is $C_6H_8O_6$),a naturally occurring water-soluble vitamin, in a molar ratio of 1:3. The initial pH of the solution was then determined, and to bring the pH to 7, aqueous ammonia hydroxide was added drop by drop to the mixed solution. A gel was formed after the liquid was evaporated at 80^0C while being agitated with a magnetic stirrer. For an additional 2 hours, the gel's temperature was raised to 120^0C.The gel quickly burns and transforms into brown powder. The resulting powder was sintered at 1000^0C to get homogeneous and pure form of nanoferrites.

This method has certainadvantagessuchas simple, lowcost, and high yield, synthesis at low temperature, control on the chemical composition, producing high quality materials, high scale homogeneity and purity, but it isdifficult to avoid residual prosperity and long processing time [20].

Co-Precipitation Method

The properties of ferrites such as structural and magnetic are observed to be receptive to their micro structural composition, which depends on the experimental environment. To manufacture nanoparticles, one has to select Chemical co-precipitation as the simplest and most convenient method. Nanoparticles can be made through Co-precipitation with least expenses and simplest approach. In the short span of time this method can produce large amounts of nanoparticles (in grams) and utilizes the most economical and easily obtainable chemicals as precursors. Nanoparticles of iron oxides can be formed through mixing of low-cost iron salts with a precipitating agent such as NaOH [21].The nucleation and growth steps are overlapped in the Co-precipitation method, but the particles are usually harvested in the time period before Ostwald ripening fully takes into effect. Figure.3 portrays usage of the Co-Precipitation method for the synthesis of the nano ferrites with the detailed flowchart.

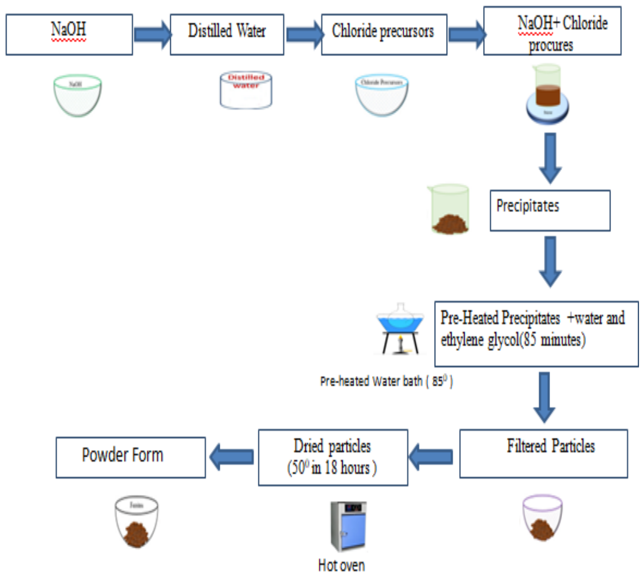

Figure 3. Flow chart for synthesis of ferrite nano particles through Co-Precipitation method.

Wet chemical co-precipitation was used to create ferrites from the MFe_2O_4 series (M = Ni, Co, Mn, and Zn). $FeCl_3$ and NaOH concentrations were both held constant during the sample, and the Fe:Na ratio was fixed at 1:4.. All the salts $MCl_2.4H_2O$ and $FeCl_3$ with different quantities were dissolved in distilled water [22]. A 100 ml solution of NaOH was poured in a beaker and stirred at room temperature using a magnetic stirrer at a speed of 50 rpm. The metallic ion solution was added drop wise to NaOH solution till the dark grey precipitate was obtained and the pH value should be maintained below 8. The beaker containing the dark grey precipitates was placed into a preheated water bath containing water and ethylene glycol. The water bath's temperature was kept below 100^0C. 85 minutes were spent on digestion. After 85 minutes, the particles finally settled to the bottom of the beaker. After being removed from the water bath, the beaker was allowed to cool to a moderate temperature. Filtration was used to obtain the particles. The filtered particles were baked for 18 hours at 50^0C to dry them out. After some time, the fine materials were produced and a powder form was made [22, 23].

This process has a number of merits, including simple particle size control, homogeneity of nanomaterial with tiny size, bulk manufacturing of magnetic nanoparticles, and energy efficiency. Traces of impurity, time consuming, and instability of the nanoparticle are some of the drawbacks of this method.

III. APPLICATIONS OF FERRITES

The most significant uses of MFe_2O_4 (M=Co,Cu,Mn,Ni, and Zn) in science and technology are shown in Figure.4. Nano - dimensional ferrites are popular magnetic materials. Multi - dimensional materials has diverse applications. Nanotechnology has a global impact on healthcare and socioeconomic development [24]. The physical-chemical characteristics of the ferrite nanoparticles have an impact on the development of potential medicinal drugs. Nanomaterial-based antiviral sprays that don't harm the environment, can be used to deliver drugs, can be used to coat household items with an antiviral surface, and can even be utilised to create biosensors for the early detection of viral strains like the COVID-19 pandemic [25]. The development of high contrast imaging dyes for viral strains in bodily fluids can be greatly helped by soft ferrites[26]. Perhaps ferrite nanomaterial developing for medicines and therapeutics, and Radar absorbing devices, magnetically recoverable for use in gas sensors, power applications, EMI, biomedical applications, energy storage applications, and multilayer chip inductors (MLCIs)[27,28].

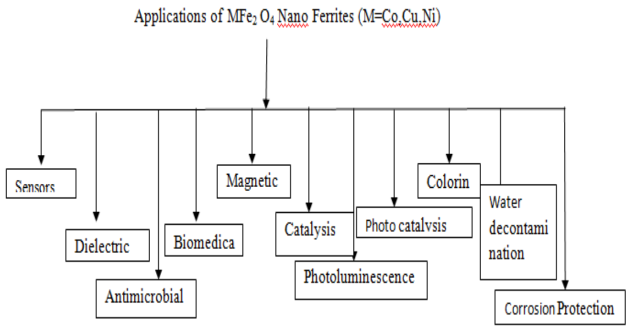

Figure 4. Applications of nanoferrites in different fields of science.

Advantages

Ferrite nano materials are chosen due to their high DC electrical resistivity, good magnetic properties, chemical stability, high permeability, wide temperature range and low eddy current losses [29], wide range of working frequency (10kHz to 50MHz), Lowest volume, highest quality, and highest stability at a low cost. Ferrites are used in In electromagnetic absorbers, microwave devices, data storage, core materials in high frequency transformers, adjustable inductors, drug delivery and delay lines. For both low-level and high-power applications, ferrites are frequently incorporated into magnetic circuits [30].

IV. RESULTS AND DISCUSSION

The properties of nanoparticles, such as particle size, structure, purity, and chemical composition, have a significant impact on the properties of ferrites. It has been demonstrated that chemical methods, such as co-precipitation, sol-gel, and hydrothermal process, effectively control the morphology and chemical composition of the produced nanoparticles. Sol-gel method involves the use of toxic organic solutions, requires very unstable alkoxides, and colloid emulsions take a long time and are difficult to maintain reaction conditions and hydrothermal reaction involves with many difficulties such as it involves slow reaction kinetics, requires high pressure reactor and expensive equipment and impossibility in observing the growth in crystal during the reaction. While one of the best methods for creating ultrafine powders with a narrow particle size distribution and pure homogeneous materials is Co-precipitation method. This procedure takes less time than alternative methods since it can eliminate difficult procedures like refluxing alkoxides.

V. CONCLUSION AND FUTURE SCOPE

It can be stated that ferrite materials are simple to synthesize, have valuable qualities, and have a variety of applications. The ferrite sensor used in the lab is a better tool for detecting viruses and measuring humidity levels. The electrical resistivity-based ferrite sensor is easy to construct, affordable, user-friendly, and suitable for both indoor and outdoor applications. However, ferrite nanoparticles have exceptional properties that they hold in a variety of fields. In the context of use of nanoparticles in the pandemic outbreak, such as in the recent COVID-19, the creation of high contrast imaging dyes for viral strains in bodily fluids can be greatly aided by soft ferrites. All of these compounds are having potential use for the electrical and electronic industrial applications. In this context, it is concluded that the co-precipitation method is found to be a promising method to prepare nano ferrites rather than that of both Hydrothermal and Sol-Gel auto combustion methods.

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