Synthesis and Characterization of Nano Strontium Ferrite and its gas sensing studies

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Abstract: Glass-Self-propagating low temperature (SPLT) route for synthesizing nanomaterials has been gaining importance in the field of synthetic technology by being a cost effective, faster and cleaner approach when compared to the other conventional and wet chemical methods for the synthesis of metal oxide nanoparticles. In the present work, synthesis of strontium iron oxide (SrFe2O3) nanoparticles viz., were carried out by SPLT route through the thermal decomposition of strontium iron metal oxalate precursors employing polyvinyl alcohol (PVA) as a fuel. The characterization was developed for size and structure by employing Fourier transform infrared (FTIR) spectral studies. The morphology of the samples ranged from nano spherical to agglomerated irregular-shaped particles for strontium ferrite samples based on the results of field emission scanning electron microscopy (FESEM) images. Possible gas sensing applications of these ferrite sample nanoparticles are studied.

Keywords: Ceramic Nanomaterials, Nano Strontium Ferrite, Self-propagating low temperature combustion, scanning electron microscopy, X-ray diffraction

1. Introduction
In an era where compactness of various devices is of prime importance, nanomaterials can play a crucial role. The properties of the commonly found materials change considerably when they are brought to nano size which is of the order of 100 nm or less and these properties can be exploited for various innovative scientific and technological applications [1]. A particular type of such nanoparticles, i.e. ceramic nanomaterials, have had a wide variety of applications. They are known for
their stability, availability of information on relatively cheaper synthesis techniques. Even with the risk of being exposed to these nanoparticles, a large number of researches are being undertaken to find new approaches to synthesize these ceramic nanomaterials and to reduce the risks involved as well [2]. Such kind of importance is given to them because of their properties which include but are not limited to functioning as catalysts, response to various stimuli to act as sensors, usage in electronic systems and in equipments where a good amount of conductance or resistance is required. Products which utilize these properties are readily available and are made for applications where sophisticated equipments are needed.

The synthesis of ceramic nanomaterials can be broadly classified into two types; top-down approach of synthesis and bottom-up approach of synthesis.

In the top-down approach, a larger piece of material is broken down into many smaller pieces. For the generation of surfaces of these smaller pieces, considerable amount of energy is required which is provided by an external source. Ball-milling is an example of this approach where the mechanical impact is the input energy for the generation of the surfaces. The balls or rods which are present in this machine provide the necessary impact which is transmitted to the material and leads to reduction in size. This is a very effective technique to produce ceramic microparticles but it is difficult to obtain nanoparticles from this technique and even if obtained, they are highly reactive and are not regular in shape. If the requirement of the ceramic nanomaterial is in small amount, another technique which utilizes the top-down approach is available which is known as nano-ablation where laser or ion beams are used to remove smaller pieces off of the larger body of material. This is only suitable for smaller requirements because of the cost involved. There are quite a few disadvantages associated with the top-down approach and among them, the primary one is the high amount of time and energy required along with the high chances of occurrence of contamination as the material is in direct contact with the machine providing the energy for reduction in size.

In the bottom-up approach, smaller pieces (atoms or molecules) of the material are combined in a controlled manner to form larger pieces (nanoparticles). The particles obtained by using this method are more stable and the size distribution is better. A wide variety of shapes can be engineered with different crystal habits. The most popular bottom-up approach techniques used are (a) Chemical vapour deposition (b) pyrolysis and (c) Sol-gel and controlled precipitation. The chemical vapour deposition is used to produce thin film of ceramics which have a good purity by exposing the substrate to a precursor which is highly volatile. In the pyrolysis technique, an organic or organometallic compound is made to undergo incomplete combustion. These are made to decompose into compounds which are highly reactive by controlling the amount of oxygen available in the combustion chamber. [3] The sol-gel method is a widely used technique for synthesis of nanoparticles which gives a good control over the stoichiometry of the material. A solution, which is normally metal alkoxide is made to undergo hydrolysis and polycondensation. With this technique, ultrafine particles can be synthesized in a relatively shorter time at lower temperatures [4].

As far as the synthesis of metal oxides of strontium is concerned, various methods have been followed by researchers to obtain the ceramic nanoparticles. Balaya, Ahrens, Kienle and Maier used the sol-gel technique to synthesize nanocrystalline SrTiO3. They were able to obtain a grain size of about 50 nm following the bottom-up approach. Characterization tests showed that there was a relatively large quantity of Ti present when compared to Sr which was discussed to be because of incomplete reactions that could have taken place. In the aqueous medium, they used a titanium foil and strontium nitrate as precursors. A mixture of ammonia solution (30%) and hydrogen peroxide (65%) was prepared and the titanium foil was dissolved in it. At a pH of 11 below 10 °C and 5 hours of stirring, the foil dissolved completely forming peroxoxytitanato acid. They continued to add EDTA in a controlled manner by adding water along with it and stirring and decreased the pH to 7 by adding nitric acid. They dissolved 1 mole of strontium nitrate in distilled water and added to this solution after stirring. The precipitate obtained after stirring for few hours was filtered and taken for centrifugal action to remove nitrate and ammonia contents upto 4 times and then heated. The heated sample ws crushed to get the powdered version of the sample. However, the nanomaterial synthesized
using sol-gel have carbon present in it in traces which cannot be avoided and there is agglomeration of particles. [5]

Using another method to synthesize the strontium ferrite nanoparticles, H. F. Lu, R. Y. Hong, and H. Z. Li could obtain particle size of about 35-50 nm. They used the method of co precipitation and studied the way in which it was affected by surfactants. They started by dissolving ferric chloride and strontium nitrate in a ration of 1:9.23 in 50 ml of deionized water. They added different surfactants into this solution to prevent the particles from getting agglomerated at a later stage. pH of this solution was maintained at 11 by adding sodium hydroxide to it. The solution was stirred at 80°C vigorously in a water bath. This led to the creation of an aqueous suspension which was gently stirred again for 30 minutes. The precipitate obtained from this was taken for centrifugal action to remove ethanol and was heated to 100°C for few hours to dry it. This was taken for precalcination for 2 hours at 400 °C. An equimolar mixture of NaCl and KCl was added to this mixture using alcohol as medium. The resulting mixture was taken to a planetary milling machine and milled for 2 hours while maintaining a speed of 40 rpm. The sample obtained from this was taken to a muffle furnace and treated at a temperature range of 600°C to 1000°C for 2 hours in order to be calcined. The sample was then cooled down to room temperature and subjected to centrifugation to remove impurities. The resulting nanomaterial was found to have grain size of 35-50 nm. [6]

Few more techniques have been mentioned by A. K. Tyagi, where he discusses the possibility of using physical and chemical vapor deposition, sputtering, inert gas condensation, molecular beam epitaxy and solution combustion method. The solution combustion process is of two steps which starts with the formation of pre-cursor and then moves to auto ignition. To get intimate blending and to prevent random redox reactions from occurring, the formation of pre-cursor is needed. A high amount of heat is generated during the process which can by a flame as well and that is the reason why it is termed as auto ignition. Glycine, urea, and citric acid are the most commonly used fuels in this method and they are chosen so that the composition of the mixture does not change and because of their low ignition temperature. The ignition is followed by generation of heat and evolution of gases. The heat generated helps in crystallization. However, a very high amount of heat is not desired as it can lead to undesirable changes the powder sample characteristics. Tyagi mixed a predetermined amount of strontium nitrate with cerium nitrate and glycine. Three cases were considered depending on the amount of fuel present and three molar ratios were given. He prepared around 8 compositions of nanocrystals of neodymia doped ceria and mixed the oxidant with the fuel by using a low quantity of deionized water. A viscous liquid was formed leading to ignition and the temperature increased upto 250 °C. A large amount of gas was produced along with some powders which was calcined at 600 °C for 30 minutes to get the required nanomaterial which is a CeO2 – SrO system. The grain size was found to be around 40-65 nm. [7]

Subrahmanyam J and Vijayakumara M discuss the self propagating high temperature combustion method which is used to synthesize powdered nanomaterials. In this process, initial reagents are ignited which leads to spontaneous formation of products. The advantages of using this method is the simple equipment associated with this method along with the lesser consumption of time and the energy which is obtained by the reaction itself. [8]

All these cited works sent their samples for characterization through Scanning Electron Microscopy to obtain surface morphology and Transmission Electron Microscopy to get particle size which was found to be less than 100 nm. The functional groups were recognized by using the Fourier transform Infrared spectroscopy.

In this work, the self-propagating method was chosen to synthesize the nanomaterial but it was done at a lower temperature of around 200 °C. The reactions were not spontaneous like the ones obtained by Subrahmanyam and Vijayakumara [8]. The reagent here was in the form of a precipitate of metal oxalate of strontium. It was continuously heated for a period of 2 hours till the moisture content disappeared and a dried sample was left behind which was used to get the powdered sample of strontium ferrite nanoparticles.
2. Materials and methods

2.1 Materials
Analytical grades of 1 N of Ammonium Iron(II) Sulphate, 1 N of Oxalic acid and 0.5 N of strontium chloride were used as primary chemicals for the synthesis. Additionally, polyvinyl chloride, in a weight ratio of 2:1 with the precipitate formed, was used as fuel and for completing the sensing studies of the sample. For a better distribution of electric current, silver paste was applied on the surface of the pellet made out of sample for Hall Effect studies.

2.2 Methods
A solution was formed by mixing 1 N of Ammonium Iron(II) Sulphate and 1 N of Oxalic acid and a yellow precipitate of metal oxalate was formed when 0.5 N of strontium chloride was mixed to it and stirred on a magnetic stirrer for 30 minutes and left to settle. The precipitate was filtered out and heated at 200 °C for 60 minutes by adding polyvinyl alcohol as fuel in a weight ratio of 2:1 with the precipitate. The heated sample was crushed in a crucible to get a fine powder of ceramic nanomaterial containing oxide of strontium.

3. Characterization Techniques

3.1 Field Emission Scanning Electron Microscopy (FE-SEM)
Field Emission Scanning Electron Microscopy was done on the sample using ZEISS Sigma field emission scanning electron microscope at an EHT of 10 kV and working distance of 7.5 mm with 2500x zoom to get the morphological characteristics of the material.

3.2 Fourier Transform Infrared Spectroscopy (FTIR)
Fourier Transform Infrared Spectroscopy was performed on the sample using Nicolet 6700 with a resolution of 4.0 cm⁻¹ getting peaks in the range of 400.1632 cm⁻¹ to 3999.7039 cm⁻¹.

4. Results and Discussion
Using the self-propagating low temperature combustion method, the ceramic nanomaterial could be synthesized in a relatively lesser time with lesser consumption of heat as it was at 200 °C.

![Figure 1 flowchart of synthesis of Nano ferrite](image-url)
4.1 Field Emission Scanning Electron Microscopy (FE-SEM)

Figure 2 shows the FESEM image of the sample obtained which was analyzed using Gwyddion software to generate a 3d visualization as shown in figure 3. The particles obtained are nearly rectangular in shape with some irregularities on the surface. The size of the particle was around 95 nm. To study the surface, further analysis was done in Gwyddion to obtain the roughness parameters.

![FESEM image of sample](image1)

![3D visualization using Gwyddion](image2)

Figure 2 FESEM image of sample  
Figure 3 3D visualization using Gwyddion

As obtained from the result, the particle under observation had an average surface roughness value of 74.05 nm.

4.2 Fourier Transform Infrared Spectroscopy (FTIR)

The first peak occurring at 3420 shows stretching of second degree amines. The next major peak occurring at 1636.82 shows 10 R-NH2 with δ NH in plane (scissoring) with stronger bond than in 2o amines. This is due to the addition of FAS while preparing the sample. Traces of the amine group are present even after the precipitate is extracted. Presence of aliphatic –C-O-C- can be concluded with the peak at 1079.63.

![Average Roughness value for the particle length](image3)

Figure 4 Average Roughness value for the particle length
Gas Sensing Applications studies

The response of a gas sensor is highly influenced by its surrounding temperature and the environment it is working in. Air was sucked out of the chamber where the sensing studies were to be undertaken before passing the gas to get more accurate results. Figures 6 shows the behavior of the sample when there is no gas present in the chamber. Figures 7, 8 and 9 show the changes occurring when the gases are being passed into the chamber. The fluctuation is in terms of voltage read over the period of time when the gas is being passed into the chamber in a periodic manner.

Figure 5 Fourier Transform Infrared Spectroscopy of the sample

Figure 6 Response without the presence of gases
Figure 7 Response in presence of acetone

Figure 8 Response in presence of ammonia
The change in the voltage read is due to change in resistance of the sample when the gas flows over it. The flow of the gas makes oxygen get adsorbed on the surface of the sample which causes this change.
in resistance. [9] The voltage reading at peaks corresponding to acetone, ammonia, methanol and ethanol were 3.62 V, 4.88 V, 4.64 V and 4.39 V respectively.

5. Conclusion
The nanomaterial of strontium ferrite was successfully synthesized using the self-propagating low temperature combustion method and characterization was done on it to get FESEM, and FTIR results and confirmed to have a grain size of around 95 nm. Sensing studies show that the sample can detect the presence of gases like vapours of acetone, ammonia, and ethanol.

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