



Chromium and copper substituted lanthanum nano-ferrites: Their synthesis, characterization and application studies



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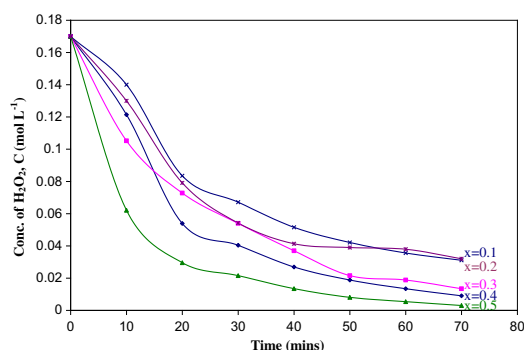
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HIGHLIGHTS

- $\text{LaM}_x\text{Fe}_{1-x}\text{O}_4$ ($M = \text{Cr}^{3+}, \text{Cu}^{2+}$; $x = 0.0-0.5$) prepared by sol-gel auto-combustion method.
- Ferrites had same symmetry as LaFeO_3 .
- Ferrites employed for catalytic decomposition of hydrogen peroxide solution.
- Cu^{2+} substituted ferrites exhibit much higher catalytic activity than pure ferrites.
- Cr^{3+} ions have little effect on catalytic activity of lanthanum ferrites.

GRAPHICAL ABSTRACT

Concentration vs time graph for decomposition of hydrogen peroxide catalysed by $\text{LaCu}_x\text{Fe}_{1-x}\text{O}_3$ annealed at 400°C .



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ABSTRACT

Nano-crystalline lanthanum ferrites substituted by chromium and copper having formula $\text{LaM}_x\text{Fe}_{1-x}\text{O}_3$ ($M = \text{Cr}, \text{Cu}$; $0.0 \leq x \leq 0.5$) were synthesized using sol-gel auto-combustion method. The formation of ferrite particles was confirmed using Fourier Transform Infra-Red (FT-IR) spectra and powder X-ray Diffraction (XRD) techniques. The entire ferrite compositions were found to be pure phased with same symmetry as LaFeO_3 . The average crystallite size was calculated to be ~ 60 nm. The ferrite compositions were observed to behave as semi-conductors, as their resistivity decreased with increasing temperature. These ferrite compositions were employed as catalysts in the decomposition of hydrogen peroxide solution (0.17 M). Pure LaFeO_3 was found to have a very low catalytic activity towards the decomposition of hydrogen peroxide solution, while presence of copper in the lanthanum ferrite lattice was found to significantly enhance its catalytic activity. The rate constant in case of reactions catalysed by $\text{LaCu}_{0.5}\text{Fe}_{0.5}\text{O}_3$ was nearly 25 times larger than that obtained from reactions catalysed by pure LaFeO_3 . However, chromium substitution was not found to influence the catalytic activity of lanthanum ferrites as chromium substituted lanthanum ferrites exhibited very low catalytic activity. This was explained on the basis of relative stability of oxidation states of the substituent ions and the presence of defects in the crystal lattice.

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Introduction

Lanthanum ortho-ferrite or lanthanum ferrite, with formula of LaFeO_3 , is a distorted perovskite-type ferrite. Its structural formula

is based upon the perovskite oxides, ABO_3 . The ionic radius of A ion is larger than 1.0 Å, while the size of the B-ion is of the order 0.6–0.8 Å [1]. It crystallizes in an orthorhombic unit cell, with Pbnm space group. Each Fe^{3+} is surrounded by six anti-parallel Fe^{3+} ions [2].

In recent years, lanthanum ferrite has attracted immense interest by virtue of its wide applications in the fields of electronic and magnetic materials. In addition, it has good catalytic and gas sensing properties. Lanthanum ferrite is also reported to be used as an electrode in solid oxide fuel cells [3]. It is also found to be visible-light photocatalytically active due to its unique opto-electronic properties and its narrow band gap [4]. In particular, the catalytic and photocatalytic properties of $LaFeO_3$ have been extensively investigated. The catalytic properties of $LaFeO_3$ are strongly dependent on grain size, method of preparation and presence of a substituent ion in the lattice.

Many attempts have been made to enhance the catalytic performance of $LaFeO_3$ by substituting lanthanum or iron ions with other metal ions. For instance, Furfori et al. [5] synthesized strontium substituted lanthanum ferrites by solution combustion synthesis method and studied the catalytic activity of these ferrites in the reduction of NO by hydrogen gas. The authors reported a significant increase in the catalytic activity in substituted lanthanum ferrites as compared to pure lanthanum ferrite. Similar substitution of $LaFeO_3$ with strontium was carried out by Ivanov et al. [6], who studied the catalytic activity of strontium substituted lanthanum ferrites in high temperature N_2O decomposition, methane combustion and ammonia oxidation reactions. The authors reported an enhanced catalytic activity in case of $LaSrFeO_3$ (surface)– $La_{0.4}Sr_{0.6}FeO_3$ composites. Pecchi et al. [7] synthesized calcium substituted lanthanum ferrites of the formula $La_{1-x}Ca_xFeO_3$ ($x = 0.0, 0.1, 0.2, 0.3, 0.4$) and tested these ferrites in the catalytic combustion of methane. The authors reported highest catalytic activity in case of $La_{0.4}Ca_{0.6}FeO_3$. Although, extensive work has been carried out in order to study the catalytic activity of lanthanum ferrites and related materials, there is still a large pool of knowledge which remains unexplored in this area.

In the present study, novel heterogeneous catalysts have been synthesized by substituting Cr^{3+} and Cu^{2+} ions in place of Fe^{3+} ions in $LaFeO_3$. Further, these catalysts have been employed in the catalytic decomposition of hydrogen peroxide solution. To the best of the knowledge of authors, the decomposition of hydrogen peroxide using chromium and copper substituted lanthanum ferrites has not been previously reported in literature. The reason for selecting the decomposition of hydrogen peroxide solution as a probe reaction for testing the catalytic activity of substituted lanthanum ferrites is the fact that the decomposition of hydrogen peroxide solution forms underlying reaction for many other processes. For instance, the decomposition of various dyes in the presence of hydrogen peroxide solution and various catalysts is an active area of research. Thus, the decomposition of hydrogen peroxide solution can be employed in various such reactions which might prove beneficial in various industrial and research applications.

Experimental

The method of preparation plays a crucial role in determining the properties of lanthanum ferrites and related compounds. Various preparation techniques have been employed to synthesize $LaFeO_3$ and related materials, including solid-state reactions at high temperature, wet chemical methods like hydrothermal synthesis, solution combustion synthesis, co-precipitation, thermal decomposition of bimetallic compounds and sonochemical method [8,9]. These methods have several problems like poor homogeneity, no control over the particle size, high porosity of samples, development of secondary phases, and lower surface area. The sol-gel auto-combustion method is a relatively good method as

it involves a simple technique and low processing temperature. It gives a good control over stoichiometry and leads to production of ultrafine particles with homogeneous distribution.

In the present work, sol-gel auto-combustion method was used to synthesize ferrite compositions having formula $LaCr_xFe_{1-x}O_3$ and $LaCu_xFe_{1-x}O_3$ ($x = 0.0, 0.1, 0.2, 0.3, 0.4$ and 0.5). In this method, the precursor nitrates [$La(NO_3)_3 \cdot 6H_2O$ (CDH Chemicals), $Fe(NO_3)_3 \cdot 9H_2O$ (Thermo Fischer-Scientific India Pvt. Ltd.), $Cu(NO_3)_2 \cdot 3H_2O$ (s.d. fine-chem limited), $Cr(NO_3)_3 \cdot 9H_2O$ (Qualigens fine chemicals)] were weighed in desired stoichiometric proportion and dissolved in minimum amount of distilled water. Citric acid (taken in the ratio metal: citric acid as 1:1) was dissolved separately in minimum amount of distilled water. The individual solutions were mixed together and the pH of resultant solution was adjusted to ~ 7 by adding dilute ammonia solution. The solution was then kept on a hot plate magnetic stirrer for 2–3 h, which resulted in the formation of gel. On continued heating, the gel self-ignited in an auto-combustion manner to yield ferrite powders, which were annealed in a furnace (in air) at temperatures of 400 °C, 600 °C, 800 °C and 1000 °C for 2 h to yield ferrite powders.

The elemental analysis of the entire ferrite compositions was carried out using an electron probe micro analyzer (EPMA) (JEOL-8000 M). The elemental analytical data for all the elements in the entire as obtained samples by EPMA were consistent within 2%. The entire ferrite samples were characterized using the Fourier Transform-Infra Red (FT-IR) spectroscopy. The FT-IR spectra were recorded on a Perkin Elmer RX-1 FT-IR spectrophotometer in the range 4000–400 cm^{-1} . Hitachi (H-7500) Transmission Electron Microscope (TEM), operated at 120 kV was used to record the micrographs of the samples. The ferrite samples were first ultrasonically agitated in absolute ethanol for 2 h. Thereafter, a drop of this microemulsion was placed on carbon copper TEM grids and dried it in air at room temperature, after which the TEM images were recorded. Powder X-Ray Diffraction (XRD) patterns were recorded using a Panalytical's X'Pert Pro spectrophotometer with $Cu K\alpha$ radiation ($\lambda = 1.5404 \text{ \AA}$). Si powder sample was used as an instrument standard and the instrumental broadening, calculated from the (111) peak was found to be 0.7 Å. Their electrical properties were studied using a two probe method. For this purpose, the ferrite sample was molded into a thin pellet. A silver paint was applied on both the surfaces of the pellet to ensure good electrical contact. The pellet was held between two electrodes of specially designed sample holder. The measurements were recorded in the steps of 10 K in the temperature range of 323–423 K (40–150 °C). The error in measurement of resistivity was approximately 3%. Further, their catalytic activity was tested in the decomposition of hydrogen peroxide solution.

The hydrogen peroxide decomposition measurements were performed by diluting 2 mL H_2O_2 solution (30% w/v) (Thermo Fischer-Scientific India Pvt. Ltd) to make the resultant volume up to 100 mL, by adding distilled water. Calculated amounts of ferrite catalyst (10 mol%, 20 mol%, 30 mol% and 40 mol%) were added to the diluted hydrogen peroxide solution. Then, 5 mL of the hydrogen peroxide solution was withdrawn at regular time intervals. It was quickly filtered through a syringe filter to completely remove the catalyst particles, and was titrated with standardized potassium permanganate solution (0.03 M), to determine the concentration of hydrogen peroxide left in solution after regular time intervals.

Results and discussion

Fourier Transform Infra-Red (FT-IR) characterization

The FT-IR spectra of perovskites are expected to exhibit two bands $\sim 550 \text{ cm}^{-1}$ and $\sim 400 \text{ cm}^{-1}$ corresponding to Fe–O

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