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Synthesis, electrical and dielectric characterization of cerium doped nano copper ferrites

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ABSTRACT

The nanosized $CuFe_{2-x}Ce_xO_4$ ($x = 0.0, 0.2, 0.4, 0.6, 0.8$) ferrites doped with cerium are synthesized by chemical co-precipitation method. The synthesized materials are characterized by XRD, FTIR, TGA and SEM. XRD analysis of cerium substituted copper ferrites confirms the cubic spinel structure. The average crystallite size calculated by using Scherrer's formula ranges from 37 to 53 nm. The values of cell constant and cell volume vary with the dopant concentration. These variations can be explained in terms of their ionic radii. The DC electrical resistivity, measured by two point probe method, increases with increase in dopant concentration while it decreases with rise in temperature exhibiting semiconductor behaviour. Energy of activation of these ferrites is calculated by using Arrhenius type resistivity plots. Dielectric measurements of the synthesized compounds show exponential decrease in dielectric constant and dielectric loss factor with increase in frequency. This indicates the normal dielectric behaviour of ferrites.

1. Introduction

For the last two decades nanomaterials (crystallite size <100 nm) have been considered the most popular emerging field of research. Many studies have been focused on the preparation of novel nanometal oxides because of their exclusive size based properties [1,2]. Similar features observed in a class of such materials, spinel ferrites, MFe_2O_4 (where M is a divalent cation) has rendered it of enormous technological and industrial importance due to their improved electrical and magnetic properties [3]. Ferrites when nanosized exhibit higher efficiency, low cost and proper dielectric loss and hence, find potential applications in memory core and microwave devices [4–6] . Moreover, they have vast applications in the fabrication of magnetics, high frequency transformers, analogue devices, antennae and radar devices [7–9]. The electrical properties of spinel ferrites depend on the method of preparation, chemical composition, grain size, doping additives [3,10,11] and the concentration of ferrous and ferric ions as well as their distribution among the tetrahedral and octahedral sites [12].

The substitution of different cations in ferrite materials induces variations in electrical properties [13,14]. The rare earth ion substitution in ferrites has been reported by many researchers to enhance their electrical and magnetic properties [15–20].

The conventional method for the synthesis of ferrites is solid state reaction method in which mixing of oxides or carbonates with intermittent grinding is followed by annealing at high temperature (1573 and 1973 K) [21]. This process of synthesis is simple yet it has many limitations such as larger particle size, less homogeneity, greater time consumption and high reaction temperature [22]. On the other hand, wet methods such as co-precipitation, sol-gel, citrate gel, micro emulsion and spray pyrolysis, produce sub-micron sized particles with high degree of homogeneity and good control of stoichiometry [3]. In the present studies, chemical co-precipitation method is selected due to its simplicity, lower cost and freedom of the synthesized material from contaminations [23].

We report the synthesis of cerium doped copper ferrites and detailed studies of their electrical and dielectric characteristics in this manuscript. Thermal, spectroscopic and microscopic characterizations of these nanomaterials are also discussed.

2. Experimental

Chemicals used in the synthesis of Ce substituted copper ferrites were $CuCl_2{\cdot}2H_2O$ (99%; Merck), $Fe(NO_3)_3{\cdot}9H_2O$ (97%; Riedel Dehaen Seelze, Germany), $CeCl_3{\cdot}7H_2O$ (98.5%; Merck) and NH_3 solution (33%; Merck).

Ferrite nanoparticles $CuFe_{2-x}Ce_xO_4$ ($x = 0.0, 0.2, 0.4, 0.6, 0.8$) have been synthesized by chemical co-precipitation method [3].

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The aqueous solutions of $CuCl_2{\cdot}2H_2O$, $Fe(NO_3)_3{\cdot}9H_2O$ and $CeCl_3{\cdot}7H_2O$ in equal volumes with their desired concentrations were mixed in a 2000 ml beaker with constant stirring and heating up to 333 K. After half an hour, 2.0 M ammonia solution was added drop wise (as precipitating agent) to the reaction mixture and the pH was kept between 10 and 11. The reaction temperature was kept at 333 K for 3 h. Precipitates thus obtained were washed with deionized water to remove the water soluble impurities. The precipitates were kept overnight in an electric oven at 373 K to remove water contents. The dried precursor was grinded to fine powder in a clean agate mortar and pestle and annealed in air at 1073 K for 8 h in an electric furnace (PLF 160/7) programmed at 5 K/min.

The structural characterization of the prepared materials was carried out by XRD analysis using Philips X'Pert PRO 3040/60 diffractometer which uses CuKα as a radiation source. The FTIR spectra of $CuFe_2O_4$ were also recorded using FTIR-8400 (Shimdzu, Japan) for structural elucidation of the synthesized compound. The thermal characterization of $CuFe_2O_4$ was carried out by TGA by using Perkin Elmer TG/DTA Diamond instrument.

JEOL-JSM-6700F field emission scanning electron microscope (SEM) was used to obtain the SEM micrographs of the synthesized compounds. For this purpose, they were mounted on aluminium stud using adhesive graphite tape and sputter coated gold before analysis. Temperature dependence of dc electrical resistivity for Ce doped copper ferrites was measured by two point probe method. The pellets used for these measurements were 0.13 cm in diameter and 0.14-0.26 cm in thickness. Dielectric measurements of the synthesized materials were carried out at room temperature in a frequency range of 100 Hz to 3.0 MHz by using the instrument (6440B, Wayne Kerr).

3. Results and discussion

3.1. Characterization

3.1.1. Thermal analysis

TGA/DTG curve of $CuFe_2O_4$ is shown in supplementary material. The 1st weight loss at 363 K in TGA curve shows the loss of free water from the copper ferrite material and has a corresponding endothermic peak at the same temperature in DTG curve. The 2nd drop in weight at 483 K can be ascribed to the elimination of hydrated water which is in agreement with the endothermic peak at about 473 K in DTG curve. A weight loss occurring in the range from 523 K to 633 K may be attributed to the removal of ammonia and nitrates adsorbed at the surface of metal hydroxides. The matching peaks for this loss in DTG curve are observed at 623 and 693 K. The conversion of metal hydroxide into oxide is indicated at 703–863 K which is represented as endothermic peak in DTG curve at 873 K. Above 863 K, no change in weight loss is observed. This constancy of the curve corresponds to the formation of pure spinel phase [24].

3.1.2. FTIR analysis

FTIR spectrum of unannealed $CuFe_2O_4$ is shown in Fig. 1a. The peaks at 449 cm^{-1}, 516 cm^{-1} and 570 cm^{-1} correspond to metal oxygen bonds. The peaks at 829 cm^{-1} and 1375 cm^{-1} correspond to N–O bending and N–O stretching vibrations, respectively, which show the presence of some residual nitrates in the synthesized copper ferrite. The other significant bands in the spectrum appear at 1604 cm^{-1} and 3500–3000 cm^{-1}. The former represents O–H bending vibrations and the latter bands correspond to O–H stretching of water present as moisture.

FTIR spectrum of annealed $CuFe_2O_4$ is illustrated in Fig. 1b. Disappearance of three peaks in the region 700–400 cm^{-1} and appearance of single peak at 599 cm^{-1} confirms the formation of pure spinel phase after annealing. The peaks at 819 cm^{-1} and 1375 cm^{-1} (corresponding to N–O bending and stretching vibrations) observed in FTIR spectrum of unannealed compound are absent in the spectrum of annealed copper ferrite material. This shows complete removal of nitrates (adsorbed at surface of the synthesized material) during annealing. The peak at 1604 cm^{-1} in unannealed material show less intensity in annealed nanomaterial at 1708 cm^{-1} depicting removed O–H bending vibrations. Similarly, peaks in 3500–3000 cm^{-1} region are also invisible showing the conversion of hydroxide into oxide on annealing. Less intense peaks in the 4000–3000 cm^{-1} region show O–H stretching

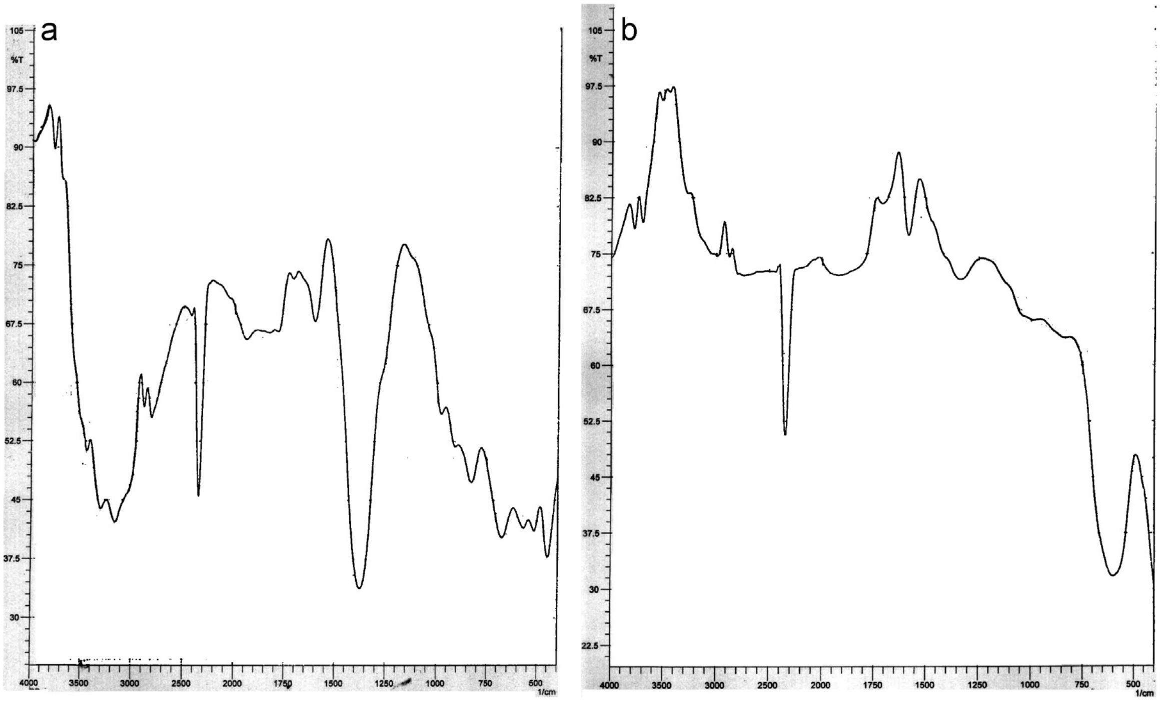

Fig. 1. (a) FTIR spectrum of unannealed $CuFe_2O_4$. (b) FTIR spectrum of annealed $CuFe_2O_4$.