Journal of Magnetism and Magnetic Materials 420 (2016) 45–50

Contents lists available at ScienceDirect

Journal of Magnetism and Magnetic Materials

journal homepage: www.elsevier.com/locate/jmmm

Investigation of superparamagnetism in pure and chromium substituted cobalt nanoferrite

M. Raghasudha [a,*], D. Ravinder [b], P. Veerasomaiah [a]

[a] Department of Chemistry, University College of Science, Osmania University, Hyderabad 500007, Telangana, India
[b] Department of Physics, University College of Science, Osmania University, Hyderabad 500007, Telangana, India

ARTICLE INFO

Article history:
Received 31 March 2016
Received in revised form
14 June 2016
Accepted 29 June 2016
Available online 30 June 2016

Keywords:
Chemical synthesis
Magnetic properties
Nanostructured magnetic materials
X-ray diffraction

ABSTRACT

Nanostructured magnetic materials with the chemical composition $CoFe_2O_4$ and $CoCr_{0.9}Fe_{1.1}O_4$ were synthesized through Citrate-gel chemical synthesis with a crystallite size of 6.5 nm and 10.7 nm respectively. Structural characterization of the samples was performed by X-ray diffraction analysis and magnetic properties were studied using Vibrating Sample Magnetometer (VSM). Magnetization measurements as a function of applied magnetic field ± 10 T at various temperatures 5 K, 25 K, 310 K and 355 K were carried out. Field cooled (FC) and Zero field cooled (ZFC) magnetization measurements under a magnetic field of 100 Oe for temperature ranging from 5–400 K were studied. The blocking temperature (T_b) for both the ferrites was observed to be around 355 K. Below blocking temperature they showed ferromagnetic behavior and above which they are superparamagnetic in nature that favors their application in the biomedical field. The substitution of paramagnetic Cr^{3+} ions for magnetic Fe^{3+} ion in cobalt ferrite has resulted in a decrease in magnetization and the coercivity of the samples. $CoCr_{0.9}Fe_{1.1}O_4$ nanoferrites with observed low coercivity of 338 Oe make them desirable in high frequency transformers due to their very soft magnetic behavior.

1. Introduction

Nanostructured magnetic materials have been the interest of the researchers in recent years due to their remarkable properties compared to their bulk counterpart. Among these, magnetic spinel nanoFerrites (MFe_2O_4) are of great importance as they exhibit novel properties that largely differ from their bulk counterparts due to the smaller particle size [1]. The magnetic and electrical properties of spinel ferrites are noteworthy. For applications of nanomaterials in different fields [2–4], new materials with improved properties than that of the existing materials need to be designed and explored.

Properties of spinel ferrites depend on the method of preparation and incorporation of different metal ions in them which induce significant changes in their electrical and magnetic properties. Due to their remarkable magnetic properties, they have a wide range of biomedical applications such as magnetically guided targeted drug delivery, magnetic resonance imaging (MRI), magnetic cell separation, etc [5–9]. Moreover, below a critical size of ~3–50 nm, magnetic properties become single domain and exhibit quite interesting magnetic properties such as superparamagnetism. In general, any ferromagnetic material converts into a paramagnetic material above its Curie temperature. Distinct to this transition, superparamagnetism is a phenomenon by which magnetic materials exhibit a behavior similar to paramagnetism below its Curie temperature. Blocking temperature (T_b) is one of the superparamagnetic properties that depend on the size of the nanoparticles. Below the blocking temperature the material shows hysteresis above which the material shows no hysteresis which is the criteria of superparamagnetism property. The area in *M–H* loop indicates the hysteresis. If it is more the hysteresis will be more. If the *M–H* loop is narrow with small area inside the loop then the hysteresis will be minimal. Superparamagnetic ferrite materials have remarkable biomedical applications such as magnetically guided targeted drug delivery in hyperthermic cancer treatment. Hyperthermia is a therapeutic procedure used to raise the temperature in an area of the body affected by cancer. Various methods are used to achieve the required hyperthermic temperature. Wide range of hyperthermia applications includes the use of radiofrequency, microwave, ultrasound or infrared. Superparamagnetic ferrite nanoparticles are most effective for non-invasive heating. Under the influence of alternating magnetic field, superparamagnetic ferrite nanoparticles are used as thermoSeed in hyperthermic cancer treatment. This is due to the fact that they can be targeted and confined to the cancer site without damaging normal cells [10]. Hence, 'superparamagnetic nanoparticles' is an important

* Corresponding author.
E-mail address: raghasudha_m@yahoo.co.in (M. Raghasudha).

http://dx.doi.org/10.1016/j.jmmm.2016.06.090
0304-8853/

research area for their biomedical applications. Specifically, nanoferrites with a crystallite size below 10 nm behave as superparamagnetic materials.

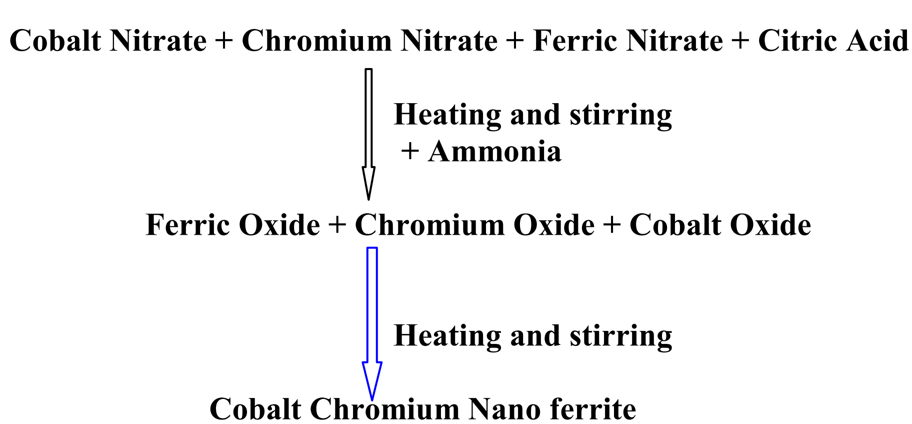
Among nanoferrites, $CoFe_2O_4$ is interesting because of its unique structural, magnetic and electrical properties [11,12]. Cobalt ferrites have been the interest of many researchers due to their high chemical stability, good mechanical hardness, moderate coercivity, moderate saturation magnetization and high electrical resistivity at room temperature. It is a medium hard magnetic material with partially inverted spinel structure in which cobalt atoms predominantly reside in octahedral sites [13]. Due to strong ferromagnetism and high Curie temperature (~740 K), Cobalt ferrites are used in electronic appliances as they allow the materials to stay magnetized even when the applied magnetic field is turned off. Thus, it leads to an effective way of information storage. Substitution of metal ions such as Al^{3+} [14], Ni^{2+} [15] and Nd^{3+} [16] in the ferrite lattice decreases the saturation magnetization and Curie temperature. Several researchers have studied and reported the effect of Cr substitution in spinel ferrites [17–19]. Substitution of Cr^{3+} ions could result in significant changes in lattice structure and is reported that Cr^{3+} ions have a strong octahedral site preference. The partial substitution of Fe^{3+} by Cr^{3+} ions in Cobalt ferrites results in a decrease in saturation magnetization and coercivity. This is due to the fact that Cr^{3+} (3 μ_B) ions have a weaker magnetic moment than Fe^{3+} (5 μ_B) ions. Thus, substitution of chromium ion in cobalt ferrite has converted the medium hard magnetic material into a very soft magnetic material favoring its applications in high frequency transformers.

Cobalt ferrites ($CoFe_2O_4$) and chromium substituted cobalt ferrites ($CoCr_{0.9}Fe_{1.1}O_4$) were synthesized via citrate-gel auto-combustion method with a very low particle size of 6.5 nm and 10.7 nm respectively [20]. Hence, these ferrites are expected to show superparamagnetism behavior. However, we could not find any reports related to the superparamagnetic behavior of chromium substituted cobalt ferrites synthesized by Citrate-gel auto-combustion method. This fact has motivated us to investigate the superparamagnetic behavior of Co–Cr nanoferrites by performing the low temperature magnetization studies in both field cooled (FC) and zero-field cooled (ZFC) modes under an applied magnetic field. The present study reports the magnetization measurements as a function of applied magnetic field (±10 T) and the temperature dependence of both field cooled (FC) and zero-field cooled (ZFC) magnetization measurements of the chromium substituted cobalt nanoferrites (synthesized by citrate-gel auto-combustion method) using the Vibrating Sample Magnetometer.

2. Materials and methods

$CoFe_2O_4$ and $CoCr_{0.9}Fe_{1.1}O_4$ nanoferrites were prepared through citrate-gel auto-combustion technique using Co $(NO_3)_2 6H_2O$, Fe $(NO_3)_2 9H_2O$, Cr $(NO_3)_2 9H_2O$, $C_6H_8O_7.H_2O$ and NH_3 as starting materials of high purity. The aqueous solutions of individual metal nitrates in the stoichiometric ratio were mixed and reacted with citric acid which acts as a fuel. The mixture was kept on a magnetic stirrer and allowed to stir continuously to get a homogeneous solution. Ammonia solution was added to adjust the pH of the solution at 7. The mixed solution was heated to about 70 °C to 100 °C on a hot plate with continued stirring that has resulted in a highly viscous gel. The gel was continued to heat on a hot plate from 180 °C to 200 °C where all the water molecules were removed from the mixture. The gel started foaming and self ignited in the hot zone of the beaker. It has resulted in a flameless auto-combustion reaction with the evolution of large quantity of gaseous products and was propagated like a volcanic eruption from the bottom to top. The total reaction was completed in only a minute resulting in a loose puffy grey powder. The obtained powder was thoroughly ground using mortar and pestle. The resultant powder was subjected to calcination in muffle furnace at a temperature of 500 °C for four hours to obtain nanosized ferrites with spinel phase. The synthesis of $CoFe_2O_4$ and $CoCr_{0.9}Fe_{1.1}O_4$ nanoferrites was shown in the flow chart given in Fig. 1.

The formation of chromium substituted cobalt nanoferrite is shown in the following chemical reaction.



The structural and morphological studies of the prepared ferrite samples were studied by X-ray powder diffractometer (XRD) and Scanning Electron Microscopy (SEM) respectively. Magnetic properties of the samples were studied using Vibrating Sample Magnetometer (VSM) in which magnetization at different temperatures was measured as a function of applied magnetic field (±10 T). To study the effect of temperature on magnetization, two types of measurements were carried out. They are, field cooled (FC) and zero field cooled (ZFC) measurements. In the ZFC process, the sample was cooled down to 5 K in the absence of a magnetic field. After the stabilization of the temperature, a measuring field was applied (100 Oe). The temperature was gradually raised and the magnetization (M) values being recorded. In the FC process, the sample was cooled in a non-zero magnetic field and the rest of