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Investigation of superparamagnetism in $MgCr_{0.9}Fe_{1.1}O_4$ nano-ferrites synthesized by the Citrate-gel method

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ABSTRACT

$MgFe_2O_4$ and $MgCr_{0.9}Fe_{1.1}O_4$ nano-ferrites were synthesized using Citrate-gel technique and the magnetic properties were studied. The crystallite sizes of the prepared $MgFe_2O_4$ and $MgCr_{0.9}Fe_{1.1}O_4$ nano-particles were estimated from X-ray diffraction patterns as 23 nm and 7.6 nm respectively. Magnetization as a function of field (± 10 T) and temperature was measured using a vibrating sample magnetometer for temperature ranging from 5 K to 300 K. From the temperature dependence of both the field cooled (FC) and the zero-field cooled (ZFC) magnetization measurements under a field of 100 Oe, blocking temperature (Tb) for $MgFe_2O_4$ was obtained at above room temperature whereas for $MgCr_{0.9}Fe_{1.1}O_4$ it was obtained at 94 K. The M–H curves for $MgCr_{0.9}Fe_{1.1}O_4$ nanoferrites indicated the presence of ferromagnetic behavior with hysteresis below the blocking temperature (T_b). A large coercive force of about 1100 Oe was found at 5 K. The phenomenon suggests that the synthesized Cr substituted Mg nano-ferrite with chemical composition $MgCr_{0.9}Fe_{1.1}O_4$ shows superparamagnetic behavior above the blocking temperature 94 K. This nature makes these materials to be used in biomedical applications like magnetically guided drug delivery and Magnetic Resonance Imaging (MRI).

1. Introduction

The unique properties of nano-scaled magnetic particles have generated more interest in the science community because these nanocrystallites have a high surface to volume ratio leading to magnetic properties contrary to those of bulk particles. Nanocrystalline spinel ferrites are currently used as key materials and exhibit unique functional applications in color imaging, catalysis [1], high density data storage [2], magnetically guided drug delivery [3], ferro-fluids [4] and magnetic refrigeration systems [5]. The field, nano-ferrites is currently the subject of research interest because of their unusual optical, electronic and magnetic properties such as superparamagnetism, low saturation magnetization, enhanced coercivity etc. [6,7]. For applications of nano-materials in various diverse fields [8–10], new materials need to be designed and explored that possess more predictable properties than the materials that are currently available. For the past few decades, $MgFe_2O_4$ has drawn the attention of researchers owing to the great potential of this material for a wide range of applications based on its unique magnetic properties [11,12]. It is very interesting that $MgFe_2O_4$ shows magnetism even though Mg^{2+} ions are non-magnetic. It may be due to incomplete inverse spinel structure of $MgFe_2O_4$ [13]. The ordering of the magnetic moments of ferric ions and the strong exchange interactions explains the excellent magnetic behavior of this material [14]. Further, $MgFe_2O_4$ belongs to a class of soft magnetic materials which is easy to magnetize and demagnetize, hence is used in electromagnets.

Below a critical size of ~3–50 nm, magnetic particles become single domain in contrast to the usual multi-domain structure of the bulk magnetic properties and exhibit interesting magnetic properties such as superparamagnetism, quantum tunneling. Normally, any ferro or ferri-magnetic material undergoes a transition to a paramagnetic state above its Curie temperature. Unlike this transition, superparamagnetism occurs below the Curie temperature of the material. The super-paramagnetic properties such as the blocking temperature and coercivity can be controlled by varying the size of the nano-particles [15]. Below blocking temperature, the free movement of the magnetic moment is blocked by the anisotropy. Above blocking temperature the system appears superparamagnetic. Superparamagnetic materials have a wide range of applications, especially their biomedical applications are noteworthy such as use in imaging (contrast agents in Magnetic Resonance Imaging-MRI) [16,17], in treatments (targeted drug delivery) [18,19] and in magnetic hyperthermia [20–22] etc. These

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specific characteristic make superparamagnetic nanoparticles a valuable research subject for considerable bio-applications. Many potential applications have been investigated and developed by researchers in the last few decades.

Nanocrystalline Ferrites with particle size specifically below 10 nm may behave like superparamagnetic materials. The nanocrystalline ferrites are being synthesized by various techniques such as sol–gel technique, hydrothermal and reverse micelle synthesis, etc. It is known that the properties of ferrites are sensitive to their compositions and microstructure which in turn are sensitive to their processing conditions [23]. It is a fact that ferrites offer immense possibilities of tailoring their various properties for various applications by doping with some metal ion. With a view to improve the magnetic properties of Magnesium ferrites for various applications, substitution of metal ion in the ferrite core is proposed. Ichiyanagi et al. [13], Chen et al. [24], Verma et al. [25] have studied the superparamagnetic behavior of $MgFe_2O_4$ synthesized by the Wet Chemical method, Co-precipitation method and mild micro-wave hydro-thermal condition respectively. Many researchers have studied the magnetic properties of the $MgFe_2O_4$ that are modified by metal ion substitution such as Ni^{2+} [26], Mn^{2+} [27,28], Cu^{2+} [29], Zn^{2+} [30], Al^{3+} [31], and Cd^{2+} [32]. Owing to the advantages of the Citrate-gel method over the other methods, Mg–Cr nanoferrites were synthesized using the Citrate-gel method with a particle size ranging from 7 to 23 nm and were reported in our earlier publication [33]. To the authors knowledge there is no information on the investigation of superparamagnetic behavior of Chromium substituted Magnesium nanoferrites. The particle size of $MgCr_{0.9}Fe_{1.1}O_4$ was found to be 7.6 nm, therefore are expected to show superparamagnetism. This has motivated us to investigate the superparamagnetic behavior of Mg–Cr nanoferrites and the present work reports the results pertaining to the magnetic behavior of $MgFe_2O_4$ and $MgCr_{0.9}Fe_{1.1}O_4$ nanoferrites.

2. Experimental

2.1. Materials

$MgFe_2O_4$ and $MgCr_{0.9}Fe_{1.1}O_4$ nanoferrites were synthesized by the Citrate-gel auto combustion technique using the following high purity chemicals.

Magnesium nitrate ($Mg(NO_3)26H_2O$, 99%, SD Fine Chem. Ltd. Mumbai, India)
Ferric nitrate ($Fe(NO_3)29H_2O$, GR grade, Otto Chemie Pvt. Ltd. Mumbai, India)
Chromium nitrate ($Cr(NO_3)29H_2O$, GR grade, Otto Chemie Pvt. Ltd. Mumbai, India)
Citric acid ($C_6H_8O_7 \cdot H_2O$, AR grade, SD Fine Chem. Ltd. Mumbai, India) and Ammonia (NH_3, AR grade, SD Fine Chem. Ltd. Mumbai, India).

2.2. Synthesis

Using the above materials nanoferrites under investigation were prepared by the Citrate-gel technique as reported in our earlier publication [33].

2.3. Characterization

The structural characterization of the synthesized samples was carried out by Phillips X ray diffractometer to investigate the phase and crystallite size using Cu Kα radiation ($\lambda = 1.5405$ Å) at room temperature by continuous scanning in the range from $2\theta^{\circ}$ to $85\theta^{\circ}$.

The Morphology of the samples was studied by Scanning Electron Microscope (SEM).

To investigate the magnetic properties of the synthesized samples containing magnetic nano-particles, the Magnetization measurements were carried up to saturation using Vibrating Sample Magnetometer [34]. From these measurements, Magnetization as a function of field (± 10 T) and temperature is measured in the temperature range of 5–300 K. To determine the temperature dependence of the magnetization two types of measurements were carried out, namely Zero-field cooling (ZFC) and field cooling (FC). According to the ZFC procedure, the sample is cooled (usually down to the liquid helium temperature) in the absence of a magnetic field and then a moderate measuring field is applied (100 Oe) and the temperature is gradually raised, the magnetization (*M*) values being recorded. The FC procedure differs from ZFC, only by the fact that the sample is cooled in a nonzero magnetic field.

3. Results and discussion

3.1. XRD analysis

The structural characterization of the synthesized nano-ferrites was carried out by X-ray diffraction analysis at room temperature. From the XRD patterns (Fig. 1) of the samples obtained by X-ray diffraction analysis crystalline phases were identified in comparison with reference data (ICSD card no. 71-1232) for $MgFe_2O_4$. All Bragg reflections have been indexed as (111), (220), (311), (400), (511) and (440) which confirmed the formation of a well-defined single phase cubic spinel structure without any impurity peak. The strongest reflection has resulted from (311) plane that indicates spinel phase. The XRD patterns of the $MgFe_2O_4$ and $MgCr_{0.9}Fe_{1.1}O_4$ nano-ferrites showed the homogeneous single phased cubic spinel belonging to the space group Fd3m (confirmed by ICSD Ref. 71-1232). The crystallite size (D) was calculated for $MgFe_2O_4$ and $MgCr_{0.9}Fe_{1.1}O_4$ nanoferrites using maximum intensity peak (311) from Scherrer's formula. Calculated Crystallite size for $MgFe_2O_4$ was 23 nm and that for $MgCr_{0.9}Fe_{1.1}O_4$ was 7.6 nm [33].

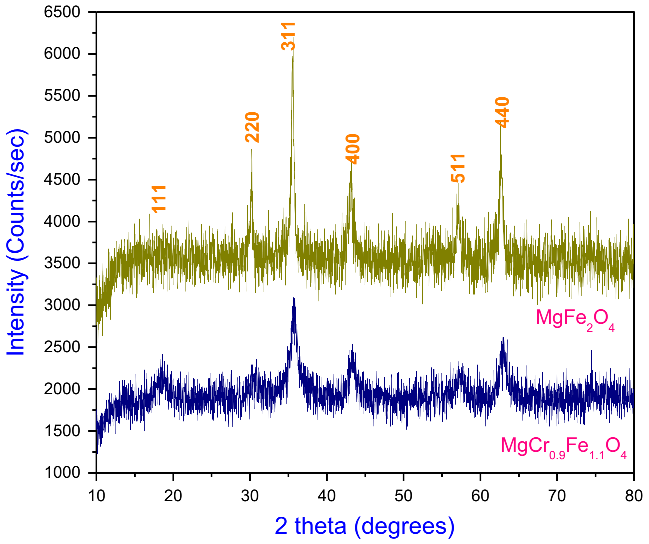

Fig. 1. XRD patterns of $MgFe_2O_4$ and $MgCr_{0.9}Fe_{1.1}O_4$ nanoferrites.