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Influence of synthesis approach on structural and magnetic properties of lithium ferrite nanoparticles

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ABSTRACT

Nanocrystalline $Li_{0.5}Fe_{2.5}O_4$ ferrite particles were synthesized with an average crystallite size of 12.3 nm and 5.7 nm by chemical coprecipitation and reverse microemulsion technique respectively. Zero-field cooled (ZFC) and field cooled (FC) magnetization measurements at different magnetic fields and magnetic hysteresis loops at different temperatures have been measured. The non-saturation of M–H loops with a very low coercivity and remenance at room temperature confirms the presence of superparamagnetic (SPM) nature and single-domain ferrite particles. The blocking temperature (T_B) has been found to shift towards the lower temperature region with the increase in applied magnetic field. It has been attributed to the reduction of magnetocrystalline anisotropy constant and blocking temperature dereases from 145 K to 110 K with increase in field from 50 Oe to 1000 Oe in the samples synthesized by microemulsion method. At high temperature, microemulsion synthesized nanoparticles show a maximum in magnetization versus temperature plot just below the Curie temperature (T_C) which has been attributed to the cumulative effect of the change in anisotropy with temperature and particle size growth during the measurement.

1. Introduction

The development of magnetic nano-crystalline materials is a subject of concern, both for the scientific value of understanding their unique properties and for the technological significance of enhancing the performance of existing materials. To meet the demand of high performance devices, an important step is to synthesize ferrites in nanoscale form. Below the critical size these nanocrystals exist in a single domain state, so that the domain wall resonance is avoided and the material can perform better at higher frequency [1]. The growing interest in ferrite is due to their chemical stability, biological compatibility, relative ease of preparation and a number of applications as an electronic material associated with them. These range from thermal and mechanical applications as sealants, lubricants and coolants to the challenging applications in medicine for the purpose of magnetic resonance imaging (MRI), targeted drug delivery, biosensors, gene transfer and magnetically mediated separation of bio-molecules [2–5]. One of the interesting application of ferrites is in hyperthermia treatment which is considered as a supplementary treatment to chemotherapy, radiotherapy, and surgery in cancer treatment [6]. The important structural, electrical and magnetic properties of ferrites are responsible for their applications in various fields. Nanophase ferrites have attracted much attention due to their technological importance in various fields, such as microwave devices, high speed digital tapes and disk recording, ferro-fluids, catalysis, and magnetic refrigeration systems. The physical properties of the nanomaterials are predominantly controlled by the surface effects than by the grains [7]. Nanocrystalline ferrites exhibit unusual magnetic properties such as single domain behaviour, superparamagnetism and reduced magnetization, which are not observed in the bulk material [8,9]. Superparamagnetism is a sole and important characteristic of magnetism in the nanosized magnetic materials. Understanding and controlling the superparamagnetic features of these ferrite nanoparticles is important for many applications. In nanoparticles the structure can substantially deviate from the bulk counter parts and depends upon the method of preparation and reaction conditions.

Easy methods to tailor nanoparticles of desired size, shape, composition, purity, and physical properties are extremely important for practical applications. Several synthesis methods have been developed to produce ferrite nanoparticles, that include hydrothermal [10], solvothermal [11], mechanical milling [12], sol–gel [13], bacterial synthesis [14] and so on. Most of them have been directed towards the preparation of particles, with a

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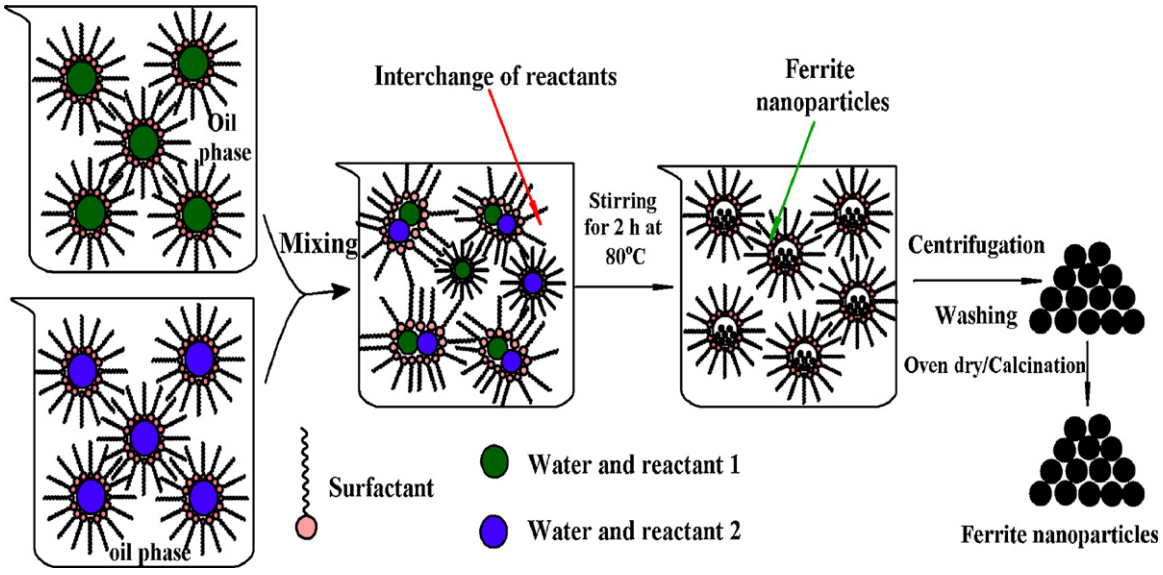

Fig. 1. Schematic representation of reverse microemulsion method for the preparation of $Li_{0.5}Fe_{2.5}O_4$ ferrite nanoparticles.

narrow size distribution in the range of few nanometers [15–17] and more recently some approaches have been experimented with the idea of achieving assemblies with suitable sizes [18–20], in particular to meet the need of biomedical applications [21,22]. However, stringent reaction conditions and complicated instrumentation in the above mentioned methods are necessary. Also the controllability of the morphology and properties of ferrite nanocrystals by these methods is limited [23]. For these reasons, it is of great importance to develop an inexpensive method to control the crystal morphology and grain size. Chemical coprecipitation, a low temperature synthesis technique is expected to control the morphology under mild reaction conditions. However, it leads to the precipitation of nanocrystals with a relatively wide range of size distribution. In order to attain very fine, monodisperse and morphologically controlled particles, a simple and efficient technique, i.e. microemulsion route has been expended in the present study to achieve the particles with desired size and magnetic properties.

Based on the surfactant-assisted strategy in aqueous media a number of methods have been developed. The surfactant plays a basic role in microemulsion, it could be taken as the ideal template for preparing nanoparticles of different shapes: spherical [24], rods [25], sheets [26], cubes [27], wires [28] and tubes [29] due to the enclosed micelles providing a space for inorganic crystal growth. Some methods are reported to give rise to the formation of either single ferrite nanoparticles [30] or to the formation of various superstructures from primary nanoparticles [15–17]. However, nothing has been reported about the conditions that can be used to produce either individual nanoparticles or their assemblies. Some workers have reported on the synthesis and fabrication of monodisperse multicomponent ferrite nanocrystals via reverse microemulsion [31,32] method, but to the best of our knowledge none of these has been devoted to the synthesis of $Li_{0.5}Fe_{2.5}O_4$ ferrite nanocrystals by reverse microemulsion method.

In the present studies we have reported the synthesis of $Li_{0.5}Fe_{2.5}O_4$ ferrite nanocrystals by chemical coprecipitation method and reverse microemulsion method. The structural and morphological analyses have been carried out by X-ray diffraction and transmission electron microscopy. The magnetic properties of the synthesized nanocrystals have been investigated by using vibrating sample magnetometer at different temperatures. Zero-field cooled (ZFC) and field cooled (FC) magnetization measurements at different fields and magnetic hysteresis loops at different temperatures have been measured. Also a comparative study of chemical coprecipitation with reverse microemulsion process has been carried out.

2. Experimental

2.1. Synthesis of $Li_{0.5}Fe_{2.5}O_4$ ferrite nanocrystals by reverse microemulsion method

All the chemicals used in this work were of analytical grade. The preparation procedure steps of $Li_{0.5}Fe_{2.5}O_4$ ferrite nanoparticles by the reverse microemulsion technique are shown in Fig. 1, with cyclohexane as oil, cetyl-tri-methyl-ammonium bromide (CTAB) as surfactant, isoamylalcohol as the co-surfactant phase. Microemulsions were prepared by adding to 10.20 g of CTAB, 12.81 ml of isoamylalcohol and 30.48 ml of cyclohexane with 5.5 wt% of an aqueous solution of the reactants, corresponding to the desired value of water/[CTAB] ratio being equal to 10.12. The emulsions were sonicated until clear solutions were formed. In order to synthesize $Li_{0.5}Fe_{2.5}O_4$ ferrite, two microemulsions were prepared: one containing the metal salts prepared by mixing stoichiometric amounts of 0.125 M $Fe(NO_3)_3{\cdot}9H_2O$ and 0.025 $Li(NO_3)_2{\cdot}6H_2O$. Second reverse micro-emulsion solution was prepared with 0.1 M aqueous solution of NaOH as water phase under similar conditions. The solutions were mixed together quickly with vigorous stirring at constant temperature (80 °C) and pH of the resulting solution was maintained at 9. The resulting solution was continuously stirred for another 2 h in order to complete the reaction. An equal volume of acetone and isopropanol was added to the resulting solution and was centrifuged to separate the solid product. The product obtained was washed several times with water and acetone followed by drying in an air oven at 100 °C for 36 h.

2.2. Synthesis of $Li_{0.5}Fe_{2.5}O_4$ ferrite nanocrystals by chemical coprecipitation method

In a typical procedure, nanocrystals of $Li_{0.5}Fe_{2.5}O_4$ ferrite were prepared by chemical coprecipitation of Fe^{3+} and Li^{1+} in an alkaline medium at constant pH of 9. The stock solutions of all the precursors were prepared with same concentration as followed in reverse microemulsion method. The stoichiometric amount of $Fe(NO_3)_3{\cdot}9H_2O$ and $Li(NO_3)_2{\cdot}6H_2O$ were mixed. Then this mixture was poured into 0.1 M NaOH solution under stirring at constant temperature of 80 °C. The resulting mixture was continuously stirred for 2 h at same temperature and pH. The resulting precipitate obtained was filtered off and washed several times with methanol and double distilled water followed by drying in an air oven at 100 °C for 36 h.

2.3. Theory

Inducing precipitation of a compound, however does not guarantee that the product will be nano-particulate, regular shaped and monodispersed. The processes of nucleation and growth govern the particle size and morphology of products in precipitation reactions. When precipitation begins, numerous small crystallites initially form (nucleation) but they tend to quickly aggregate together to form larger, thermodynamically more stable particles (growth). To produce nanoparticles, the nucleation process must be relatively fast in comparison to the growth one. The formation of particles with a narrow size distribution requires that the nuclei of all species should form simultaneously and inhibiting subsequent nucleation of smaller