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Synthesis and characterization of uniform fine particles of pure and chromium-substituted manganese ferrite with low dielectric losses

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ABSTRACT

Pure and chromium doped manganese ferrite ($MnCr_xFe_{2-x}O_4$ with x=0.0, 0.2, 0.6, 1.0) uniform particles were synthesized by chemical precipitation in surfactant-free aqueous medium and characterized by various physical techniques such as SEM, XRD, EDX, TG/DTA, FTIR and LCR meter. Our results showed that calcination up to 1100 °C could not initiate a single phase formation and particle morphology was distracted in case of undoped sample. However, replacement of some of Fe^{3+} ions with Cr^{3+} ions resulted single spinel phase with controlled morphology and lowered ferritization temperature. This effect was attributed to the increased ion mobility, which led to the enhanced solid-solid interactions between the metal oxides in the solid matrix. The crystallite size of the calcinated products was found to increase linearly with increase in calcination temperature and Cr^{3+} content in the solid sample. Various crystallographic properties were calculated for the selected solids, which are discussed on the basis of difference in the ionic radii of the replacing ions. Dielectric parameters showed relaxation behavior with frequency beyond 2 GHz. AC conductivity study showed involvement of small polarons in conduction mechanism. The significantly lowered dielectric losses and high quality factor enable the synthesized material to be used in hi-tech applications.

1. Introduction

Manganese ferrite ($MnFe_2O_4$) is considered an important member of the spinel ferrite family, which has an edge over other ferromagnetic materials due to its high electrical resistivity and low eddy current losses. They have captivating application in electronic & telecommunication, high-density magnetic recording, computer memory chips, magnetic refrigerators, inductance components, radio frequency coil fabrication, switching devices, microwave devices, transformer cores, ferro-fluids, sensor technology and use as catalyst or catalytic support [1–5]. They are also appreciated in biomedical field for magnetic drug delivery [6] and as a MRI contrast agent [7] etc. In these applications, microstructure, morphology and uniformity in particle size of ferrite nanoparticles momentously affect their performance. Consequently, control over the particle shape and size of particles is essential during its synthesis for producing ferrite powder, composed of particles with identical morphological features. Conventionally, ferrites are prepared by ceramic process, which involves solid-state reactions at high temperatures of up to 1700 °C and yields polydispersed particles of larger size [2,8,9]. Moreover, due to mechanical mixing of the starting stuff, this method encounters the difficulty of specifying traces of the dopant additives [2]. Chemical methods have also been employed being, chemical coprecipitation preferred due to its several advantages over other methods in simplicity, product purity, cost effectiveness, homogeneity and better control over the particle size [10]. However, due to anisotropic dipolar interactions, the ferrite nanoparticles can face aggregation, which are the least likely thing to happen and prevention from aggregation is necessary to achieve genuine results in powder-based technologies. Surfactants are usually used to prevent agglomeration but the leftover surface-adsorbed surfactants may led to irregular impact on particle's toxicity and reduce access to the surface of the particles. The later cause a serious issue in gas sensing and catalytic applications [11].

The powder obtained by the coprecipitation method comprised of corresponding metals hydroxides that need high temperature treatment get to the desired spinel crystalline phase. Very high temperature treatment often initiates abnormal grain growth, which degrades the power loss characteristic of ferrites [12]. Alternatively, the introduction of small amounts of the third metal into the M^{2+} and Fe^{3+} solid solution results in decrease of

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calcination temperature, particle size and significantly alter the electro-magnetic properties of the synthesized ferrites [2,13]. It is noteworthy that the electromagnetic behavior of the Fe^{3+} in ferrites can be tuned by introducing a metal that are either of a smaller atomic radius [14] such as chromium, or of higher electronegativity than iron like rhodium [15]. Researchers have successfully doped various metals into the matrix of Mn ferrite like Mg^{2+} [16], Li^{+} [17], Ni^{2+} [18,19], Zn^{2+} [20], Ti^{4+} [21], Cd^{2+} [22], Cu^{2+} [23,24], In^{3+} [25], and rare earth metals [26]. On the other hand, Cr^{3+} has also been reported to enhance the electro-magnetic properties of various ferrite systems [27–32] However, studies on the doping of Cr^{3+} ions into Mn ferrite uniform nanoparticles and their impact on microstructural, morphological, electrical and dielectric behavior are rare.

Therefore, this work is devoted to present a facile, surfactant-free coprecipitation route for the synthesis of plain and chromium doped manganese ferrite monodispersed particles. The crystallochemical aspects including phase structure, crystallite sizes, and lattice parameters were carefully investigated. Moreover, the dopant-induced enhancement in the morphological, electrical and dielectric properties of the materials has been investigated.

2. Experimental

2.1. Materials

Chemicals used in this study were $Fe(NO_3)_3 \cdot 9H_2O$ (Scharlau), $MnSO_4$ (Scharlau), $Cr(NO_3)_3 \cdot 9H_2O$ (ACROS), HCl (Riedel-de-Haer), and NH_4OH (BDH England). These chemicals were of analytical grade and employed as such without further purification. All the stock and working solutions were prepared in de-ionized water. Pyrex glass vessels were utilized for solutions preparation, storage and for carrying out the reaction.

2.2. Synthesis of plain and Cr-doped manganese ferrite

For this purpose, aqueous solutions containing various volumes of $Fe(NO_3)_3 \cdot 9H_2O$ (0.2–0.6 mol/L) and $MnSO_4$ (0.1–0.3 mol/L) were mixed in appropriate ratios in the absence and presence of 0.01–0.05 mol/L $Cr(NO_3)_3 \cdot 9H_2O$.The mixtures were heated at various temperatures from 30 to 90 °C in a double walled Pyrex glass vessel connected to a circulatory water bath (WiseCircu WCB-6) under constant stirring on a magnetic stirrer (WiseStir MSH-20D). The pH of each of the reaction mixtures was adjusted to be close to 12 by the addition of 3 M NH_4OH. The precipitates formed were stirred for 3 h at room temperature, aged overnight, and washed several times with distilled water until a pH of 7 was obtained. In each case, the precipitate was dried in an electric oven (BINDER FD53) at 100 °C and stored in tightly capped sample bottles for further characterization.

2.3. Heat treatment

Selected batches of the as-prepared solids were heated in a programmable furnace (Nabertherm, M7/11) at different temperatures (600–1100 °C) at the rate of 10 °C/min for a period of 1 h. The samples were removed from the furnace after room temperature was reached and stored in desiccator.

2.4. Characterization

Morphology of samples the was examined through scanning electron microscope (JSM-5910, JEOL). Powder X-rays diffractometer (PANalytical, X′pert PRO, Netherlands) with CuKα radiations source, was used for assessing crystallinity of the test materials. Elemental and thermal analyses of the desired samples were conducted using energy dispersive X-ray spectrometer (INCA-200, Oxford) and Diamond TG/DTA Perkin Elmer analyzer, respectively. For functional group analysis, the samples were subjected to Fourier transform infrared spectrophotometer (IR Prestige-21 FTIR-8400, Schimadzu) in the wave number range of 400–4000 cm^{-1}. Dielectric measurements were performed on pelletized samples, coated with highly conducting silver paint, using Agilent 4287 A RF LCR meter in the frequency range of 1 MHz to 2 GHz at room temperature.

3. Results and discussion

3.1. SEM analysis

Manganese ferrite particles were synthesized by the surfactant-free chemical coprecipitation method. Experimental parameters such as precipitating agent, reactants concentration, and reaction temperature were optimized as these are the major factors to control the properties of the precipitated solids. A series of Cr^{3+} doped manganese ferrite particles ($MnCr_xFe_{2-x}O_4$ with x=0.2, 0.6 and 1.0) were synthesized using the set of optimal experimental conditions (Fig. 1A) according to the generalized reaction 1:

$$Mn^{2+} + xCr^{3+} + 2 - xFe^{3+} + 8\bar{O}H \xrightarrow{80\,^{\circ}C} Mn(OH)_2 \downarrow + xCr(OH)_3 \downarrow + 2 - xFe(OH)_3 \downarrow \quad (1)$$

The as prepared undoped particles (MF-0) were given heat treatment at 600, 750, 850, 1000 and 1100 °C and were then analyzed with SEM to look for annealing induced morphological changes. Fig. 1B–F shows that heat treatment did affect the particle morphology of this material. In general, the extent of particle aggregation increased with the increase in calcination temperature, which has also been reported in the literature [33,34]. We believe that as the temperature increases, the grain boundaries come closer and closer until several particles fuse to form a single large particle. At 1000 °C and above, we noticed a substantial grain growth, which pointed to the endothermic nature of the particles aggregation process. The same type of temperature dependent particles growth/enhanced aggregation behavior of ferrites was observed by other researchers [34–36].

Partial substitution of Fe^{3+} with Cr^{3+} ions in the MF-0 sample was found to enhance the solid-solid interactions thereby controlling the particles morphology during the course of heating. SEM images of the variously doped particles calcined at 1000 °C for 2 h in air atmosphere are shown in Fig. 2. Inspection of the micrograph shows that the spherical particles have been transformed into poly-faced large particles with heat treatment [36]. It is worth mentioning that the presence of dopant in the tested sample also inhibited the abnormal grain growth during the heat treatment.

3.2. EDX analysis

In order to confirm the successful precipitation of the targeted material, two typical samples i.e., MF-0 and $MnCrFeO_4$ particles were analyzed by Energy Dispersive X-ray spectroscopy (EDX) Fig. 3. Elemental analysis of the as prepared particles indicated the presence of Mn, Fe, O and Mn, Cr, Fe, O in pure and doped samples, respectively. The ratio of the constituent elements, determined qualitatively with EDX was in close agreement with the initial stoichiometry of iron and manganese in the precursor reactant mixture of the d sample. This showed that the optimized composition of the starting reactant mixture proved suitable for the

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