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Systematic study of Ce^{3+} on the structural and magnetic properties of Cu nanosized ferrites for potential applications

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ABSTRACT

Ce^{3+} substituted Cu-spinel nanoferrites $CuCe_xFe_{2-x}O_4$ (x = 0.00, 0.02, 0.04, 0.06, 0.08 and 0.10) were synthesized via sol–gel self-combustion hybrid route. Single phase spinel ferrite of Cu nanoferrites were examined using X-ray diffraction (XRD) analysis whereas the multiphase structure was observed as Ce contents increased from x = 0.06. Field emission scanning electron microscopy (FESEM), Thermogravimetric and differential thermal analysis (TGA and DTA) and Fourier transform infrared spectroscopy (FTIR) were used to find out the morphology phase and metal stretching vibrations of Ce^{3+} substituted nanocrystalline ferrites. The crystallite size was increased and found in the range of 25–91 nm. The agglomerations in Cu ferrite samples increase as the Ce^{3+} concentration increases. The magnetic properties such as remanence, saturation magnetization, coercivity, Bohr magneton and magnetocrystalline anisotropy constant (K) were determined using M–H loops recorded from a vibrating sample magnetometer (VSM). Saturation magnetization, remanence and coercivity are increased as the Ce^{3+} contents increase in Cu nanocrystalline samples. Moreover, law of approach to saturation (LoA) was used to calculate the maximum value of saturation for Ce-doped Cu nanoferrites. The soft magnetic behaviour of the Cu nanoferrite is observed as compared to the samples substituted with the increased Ce contents in Cu nanocrystalline ferrite. Bohr magneton and magnetocrystalline anisotropy are found to increase with the substitution of rare earth Ce^{3+} contents in Cu spinel nanocrystalline ferrite. Ce-doped Cu nanocrystalline ferrites with excellent properties may be suitable for potential applications in sensing, security, switching, core, multilayer chip inductor, biomedical and microwave absorption applications.

1. Introduction

Magnetic nanoferrites have been paid much attention due to their potential and versatile technological industrial applications in many fields. Spinel ferrites are important magnetic materials because of their excellent structural, mechanical, morphological, chemical and magnetic characteristics.[1,2] Currently, magnetic nanoferrites have been used in biomedical, electronics and industrial fields for their potential applications such as target drug delivery, magnetic resonance imaging, oscillators, filters, magnetic switches, magnetic transformer cores, multi-layer chip inductors (MLCIs), high-density data storage, magnetic ferrofluids, high sensitive sensors, antennas, magnetoelectric domain switching, microwave absorbers and high frequency devices and their components.[3,4] The crystal structure of spinel nanoferrites with cubic structure of oxygen ions consists of 32 octahedral sites (B) and 64 tetrahedral sites (A). However, metal cations occupy the 16 octahedral sites and 8 tetrahedral sites. Therefore, most of the interstitial sites are empty in the spinel structure for the cations.[5] The properties of the spinel nanoferrites are strongly dependent on the chemical composition, preparation, morphology, crystallite size, lattice strain, dopants, distribution of metal cations on the lattice sites and sintering temperature.[6]

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Moreover, spinel nanoferrites have better chemical and physical properties because of their thermal stability, large surface to volume ratio, surface anisotropy, super paramagnetic behaviour, spin canting, Debye temperature, lattice strain, dislocations of atoms in crystal lattice and accumulation of atoms at grain boundaries.[7–9] The soft and hard character of the nanoferrites play an important role for their use in different applications such as biomedical for target delivery, adsorption, recording, data storage and MLCI's. Therefore, it is essential to tune the properties of the nanoferrites according to the requirements. The magnetic properties can be tailored by making variation in the chemical composition, concentration, size of particles, controlled morphology and magnetic phases in the magnetic materials.[10]

Therefore, it has been of great interest for the scientist to prepare new magnetic nanoferrites with better electric and magnetic performance which results in variety in structural and magnetic properties for versatile applications. Various investigations introduced that the substitution and sintering process are very effective and can control the structural and magnetic properties of the nanoferrites.[11–13]

A small amount of doping of rare earth ions in the ferrite structure can tune and improve the structural, morphological and magnetic properties of the magnetic nanoferrites. The properties of the nanoferrites depend on the type of cations and the distribution of the metal cations on the lattice sites. The previous studies also revealed that the combination of Ce rare earth ions and transition metal ions along with Fe ions in spinel structure may produce excellent magnetic properties for variety of applications. Different researchers have adopted different techniques for the preparation of spinel nanoferrites. In recent years, chemical wet methods have been used to synthesize the spinel nanoferrites because of their better final products. The synthesis techniques include hydrothermal, microwave method, self-combustion, sol–gel, sol–gel auto combustion, mechanical alloying, glass crystallization method, co-precipitation methods.[14–18] Sol–gel technique has been found better due to their fine surface morphology, low temperature synthesis, excellent properties and better homogeneity of mono dispersed particles.[19]

Cu ferrite has cubic close packed structure with tetrahedral and octahedral sites lattice sites (A and B sites) respectively. The electromagnetic properties depend on the position ionic radii and the distribution of the metal cations on the lattice sites respectively. The exchange of electrons during Fe–Fe interaction on the A and B sites produce changes in the properties of the nanoferrites. However, rare earth ions along with the Fe and metal transition may result in unique properties.[20] In this context, Ce is used in Cu ferrites due to many functional active sites and large surface area.[21] To the best of our knowledge, a few researchers discussed the role of Ce in Cu ferrite. However, the systematic study of Ce contents on Cu spinel nanoferrites related to their structural and magnetic properties are not evaluated. Moreover, the detailed magnetic analysis for this nanoferrite system is also not studied yet.

In the present study, we have synthesised Ce-doped copper nanoferrites using sol–gel technique. The prepared nanoferrites were characterized by different experimental techniques such as X-ray diffraction analysis, FESEM and VSM to find out the structural, morphological and magnetic characteristics. The Law of approach to saturation was applied to investigate the saturation magnetization data. The main objective of doping Ce in Cu ferrite system is to improve the properties including structural, morphological and magnetic of spinel ferrites for a variety of applications such as core, filters, phase shifters, circulators, switches, electromagnetic compatible devices and multilayer chip inductors (MLCI's) components and devices fabrication.

2. Materials and methods

2.1. Materials

Copper nitrate ($Cu(No_3)_3\cdot H_2O$), cerium nitrate ($Ce(NO_3)_2\cdot 6H_2O$), iron nitrate ($Fe(NO_3)_3\cdot 9H_2O$), citric acid ($C_6H_8O_7$) and nitric acid (HNO_3) (purity 99.99%) were used to synthesize the $CuCe_xFe_{2-x}O_4$ ($x = 0$, 0.02, 0.04, 0.06, 0.08 and 0.10) nanoferrites.

2.2. Preparation of samples

The $CuCe_xFe_{2-x}O_4$ (x = 0.00, 0.02, 0.04, 0.06, 0.08 and 0.10) ferrite samples for CuCe spinel system were prepared using sol–gel self-combustion hybrid route. The metal nitrates (with purity of 99.99%) of copper nitrate $Cu(No_3)_3\cdot H_2O$, cerium nitrate ($Ce(NO_3)_2\cdot 6H_2O$) and iron nitrate ($Fe(NO_3)_3\cdot 9H_2O$) were dissolved in HNO_3. Molar ratios of the citric acid to nitrates were kept at 3:1. The ammonia was added to maintain the value of pH at ~8. The citric acid ($C_6H_8O_7$) was used as a fuel due to low ignition temperature and better complexion ability as compared to others fuel used for the sol–gel derived methods. The mixed solutions were stirred on a stirrer at 250 r/min for 2 d. The stirred solutions were heated on the hot plate stirrer from room temperature to 80 °C with gradual increase in temperature and allowed to form gel. The viscous brown gel was then combusted on the hot plate stirrer by increasing temperature from 80 to 110 °C. The combusted gel was dried in an oven at 120 °C for 48 h for further removal of moisture. The dried powders were ground for 6 h to get the fine powders of Ce-doped Cu nanoferrites. All $CuCe_xFe_{2-x}O_4$ (x = 0.00, 0.02, 0.04, 0.06, 0.08 and 0.10) samples were sintered at 750 °C for 6 h with sintering conditions of 1–20 °C/min using muffle furnace.

2.3. Characterizations

X-ray diffraction patterns for $CuCe_xFe_{2-x}O_4$ (x = 0.00, 0.02, 0.04, 0.06, 0.08 and 0.10) samples were taken using X-ray diffractometer (Bruker D8 advance). The Cu Kα radiation with wavelength of 0.15406 nm was used. The scanning rate or step size was 0.05°/s respectively. The phase, crystalline structure, and purity of Ce-doped Cu nanoferrites samples were determined from the XRD patters. In addition to this, various other parameters such as inter planer spacing '*d*', theoretical and experimental lattice parameters, hoping lengths at lattice sites (bond lengths), the mean ionic radii of A and B sub lattices (R_A and R_B) were also calculated using XRD data. Fourier transform infrared spectroscopy was used to find out the phase, structure and vibrational bands information. The FTIR analysis was done using KBr pellet method with a Shimadzu 8400S IR spectrometer. Thermogravimetric and differential thermal analysis was also done for the prepared samples. The morphology and grain size were calculated using FESEM (SUPRA 55VP ZEISS). The room temperature magnetic properties such as remanent magnetization (M_R), saturation magnetization (Ms) and coercivity (Hc) of CuCe nanocrystalline ferrites were calculated using VSM-model LakeShore/7404. In addition, LoA (Law of approach to saturation) was applied to M–H loops for the determination of the maximum saturation magnetization of Ce-doped Cu nanoferrites samples.

3. Results and discussion

3.1. Materials characterization

3.1.1. X-ray phase analysis

The staked XRD patterns of $CuCe_xFe_{2-x}O_4$ (x = 0.00, 0.02, 0.04, 0.06, 0.08 and 0.10) nanoferrite samples are depicted in Fig. 1. The phase, structure, crystallite size, lattice parameter and cell volume