Debye temperature and elastic properties of Mg-doped cobalt ferrite nanoparticles synthesized via green approach

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Abstract. In this study, magnesium doped cobalt ferrite ($Co_{0.75}Zn_{0.25}Fe_2O_4$) nanoparticles were synthesized using sol-gel combustion using green (black pepper) extract as a chelating agent and metal nitrates as a metal source without using organic chemicals. Here, eco-friendly, inexpensive, and easily fabricated composite Co-Mg ferrite, was introduced with the role of biofuels and their advantages Fourier transform infrared spectroscopy (FTIR) was investigated to study their elastic and magnetic properties. The higher frequency absorption band at wavenumber ($\nu_2 \approx 534$ cm-1) (ν_1) is caused by scratching vibrations of the tetrahedral metal-oxygen bond and lower frequency absorption band (ν_2) at wavenumber ($\nu_2 \approx 410$ cm-1) is caused by metal-oxygen vibrations in octahedral sites. The various elastic parameters were found from FTIR analysis including tetrahedral mass (m_A), octahedral mass (m_B), tetrahedral vibrational frequency (ν_1), octahedral vibrational frequency (ν_2), tetrahedral force constant (k_t), octahedral force constant (k_o), Debye temperature (Θ_D), average force constant (k_{avg}), lattice constant (a), elastic stiffness constant (C_{ij}), stiffness constant (C_{il}), Young's modulus (Y), Bulk modulus (B) and modulus of rigidity (R).

1. Introduction

Ferrites are oxides that exhibit remarkable magnetic properties and have been investigated for five decades. Over the years, ferrites have been extensively studied for their special properties, making them one of the most interesting multifunctional materials. Its fascinating chemical, electrical, dielectric, and magnetic properties have made spinel ferrites an important electronic and magnetic material. Ferrites have been subjected to countless studies for a variety of purposes[1]. Ferrites are highly stable, non-toxic, highly compatible, and remain the backbone of magnetic and electrical engineering and technology due to their widespread application in transformers, magnetic storage devices, and other technological applications[2, 3]. The treatment of polluted water has also been achieved with them. There are two types of spinel ferrite $(A^{2+})[B_2^{3+}]O_4^{2-}$, in which A^{2+} and B^{3+} are divalent and trivalent cations, respectively, which occupy tetrahedral (T_A) and octahedral (O_B) interstitial metallic sites throughout the fcc lattice completed by O^{2-} ions. In contrast, in inverse spinel ferrite, T_A sites are occupied by trivalent cations while O_B sites contain both divalent and trivalent. However, in mixed valent inverse spinel ferrites, both sites can be filled by divalent and trivalent cations, including monovalent cations [4]. A special class of magnetic materials, nanocrystalline spinel ferrites, has emerged in recent years with applications in medical diagnostics, MRI imaging contrast agent, magnetic hyperthermia, treatment of cancer, sensors (gas, electrical and magnetic), agriculture, miniaturization of antenna, digital printing, magnetic drug delivery and biomedical research etc. [5, 6]. In addition to their high magnetic anisotropy and spontaneous magnetization, nanocrystalline superparamagnetic compounds are considered an effective material for hyperthermia, relaxometry, and contrast agents in MRI. The magnetism of cobalt ferrite (CoFe2O4), one of the important members of the spinel family, has gained renewed interest under its unique mechanical and physical properties. Biomedical applications can benefit from its excellent physical and chemical stability, substantial anisotropy and saturation magnetization, and tunable coercivity. Furthermore, they are also enhanced by Mg substitution [7]. Mg-ferrite is a highly catalytic material with high magnetic permeability as well as a high humidity and gas sensor. Magnesium ferrites are highly resistant, have a high Curie temperature, and are environmentally stable, so they are excellent candidates for an extensive range of applications [8]. Researchers have studied and processed several ferrites using a variety of methods, such as co-precipitation, sol-gel combustion, modified oxidation, forced hydrolysis, hydrothermal process, ball-milling, aerosol method, and the solid-state method. For the preparation of high-quality nano ferrite samples and tuning their chemical, optical, and magnetic properties by cationic substitution at metal sites, special efforts have been made in the past two decades using eco-friendly green synthesis routes[9]. Currently, nanotechnology is focusing on improving nanoparticles synthesis methods to make them more efficient, simple, and clean, which tends to reduce environmental pollution. Biogenic routes are attractive alternatives to traditional methods. They use nontoxic, biocompatible, relatively reproducible reagents, are environmentally friendly, and yield superior materials. Nanoscience research incorporates principles of green chemistry derived from plants, yeasts, fungi, and bacteria. The integration of green chemistry into nanoscience is a key issue[10]. With plant extracts from leaves, flowers, roots, or seeds, it is possible to prepare nanostructured magnetic ferrites with several chemical pathways using benign reagents, thus reducing the risk of hazardous substances. The plant extracts contain and can therefore release a variety of metabolites including carbohydrates, polysaccharides, phenols, amino acids, and vitamins, which can actas capping agents, reducing agents, and stabilizing and/orchelating agents for "capturing" the metal ions; they can alsoplay a fuel role. The synthesis of nanoparticles with plant extracts can influence their size, shape, and morphology. They have a wide size distribution, a high disparity, and high stability. [11-13]. Nowadays, a variety of plant extracts such as Aloe-Vera leaves, ginger roots, and Hibiscus rosa-sinensis flowers and leaves are used to obtain metal oxides and mixed oxide nanoparticles[14, 15]. The local symmetry of crystalline and noncrystalline solids was determined using infrared spectroscopy, and the ordering phenomenon was investigated in ferrites using infrared spectroscopy. IR absorption bands are primarily caused by oxygen ion vibrations with cations at various frequencies[16]. Several factors influence the frequencies of spinel ferrites, including their cation masses, lattice parameters, and cation-oxygen bonding, for example. Elastic properties of spinel ferrites have not been investigated as thoroughly as their magnetic and electrical properties. The present work aimed to estimate Co-Mg ferrite's elastic properties using IR to study the elastic behavior of these ferrites[17]. Furthermore, there is a necessity to study the elastic behavior of these ferrites with new compositions possessing desired elastic properties. In the literature, there are reports on the elastic properties of Co-Mg ferrites; the present communication is an attempt to synthesize $Co_{1-x}Mg_xFe_2O_4$ (where x = 0.25) using eco-friendly green synthesis. For the first time, we have described how we used black pepper extract as a chelating agent to systematically report Mg substitution in Co ferrite and studied their elastic properties.

2. Experimental details

2.1. Chemicals

A simple method for preparing cadmium substituted cobalt ferrite nanoparticles has been developed using analytical grade chemicals obtained from Merck, India. Analytical grade chemicals obtained from Merck, India, are used to prepare cadmium substituted cobalt ferrite nanoparticles. Cobalt nitrate [$Co(NO_3)_2{\cdot}6H_2O$], ferric nitrate [$Fe(NO_3)_2{\cdot}9H_2O$], magnesium nitrate [$Mg(NO_3)_2{\cdot}6H_2O$], and ammonia (NH_3) is used for the preparation of the $Co_{075}Mg_{0.25}Fe_2O_4$ nanoparticles by green synthesis method. There was no further purification of the chemicals. Ammonia (NH_3) was used to maintain the pH of the solution.

2.2. Preparation of Black pepper (Piper nigrum) extract

We prepared bio-extracts using fine powder black pepper powder (Piper nigrum). Seven grams of black pepper powder were dissolved in 50 ml distilled water and the mixture was boiled for 30 minutes with magnetic stirring. Afterward, the filtered extract was used for further synthesis after it was cooled at room temperature

2.3. Preparation of $Co_{075}Mg_{0.25}Fe_2O_4$ ferrite nanoparticles

Black pepper (Piper nigrum) extract was used as the fuel for the sol-gel auto combustion method to make $Co_{075}Mg_{0.25}Fe_2O_4$ nanoparticles. The Cobalt nitrate [$Co(NO_3)_2{\cdot}6H_2O$], ferric nitrate [$Fe(NO_3)_2{\cdot}9H_2O$], and magnesium nitrate [$Mg(NO_3)_2{\cdot}6H_2O$] were dissolved in 300 ml of distilled water with continuous stirring for 15min. To avoid toxic chemicals, black pepper extract (Piper nigrum) was added as an eco-fuel. Ammonia solution was used to maintain pH at 7. On a hot plate, the solution was continuously stirred and heated for approximately two hours at 80-90°C. After the production of the sol-gel, a very viscous gel, the temperature was raised to 120 °C so that the dried gel could be ignited, and powder could be obtained. As a result of burnt ash, Co-Mg ferrite nanoparticle powder is ground into a fine powder. This powder is then sintered for four hours at 600 °C to eliminate any remaining impurities. The sintered sample is again ground and used for further characterization with CMF2 coding.

2.3. Characterization tools

The $Co_{075}Mg_{0.25}Fe_2O_4$ nanoparticles were characterized by using Fourier transform infrared spectroscopy (FTIR). The vibrational modes were identified by the Shimadzu FT-IR System in the wavenumber range of 380–4000 cm^{-1}. The analysis determines various elastic parameters.

3. Results and discussion

3.1. Fourier transform infrared spectroscopy (FTIR)

Figure 1 illustrates the FTIR absorption bands of $Co_{075}Mg_{0.25}Fe_2O_4$ ferrite systems, which were recorded at room temperature in the wavenumber range of 380-4000 cm^{-1}. FTIR spectroscopy is an important and non-destructive tool that provides qualitative details regarding crystal structures of materials. According to this description, the first absorption band at this wavenumber ($\nu_1 \approx 534$ cm^{-1})corresponds to the intrinsic vibrations of the tetrahedral complexes with the highest restoring force. The higher frequency absorption band (ν_1) is caused by scratching vibrations of the tetrahedral metal-oxygen bond and lower frequency absorption band (ν_2) at wavenumber ($\nu_2 \approx 410$ cm^{-1})is caused by metal-oxygen vibrations in octahedral sites.Table2 displays the absorption band edges, tetrahedral (k_t), and octahedral (k_o) force constants of the samples. According to Waldron's method, force constants are calculated using the following equations:

$$k_t = 4\pi^2 c^2 \nu_1^2 M_A \tag{1}$$

$$k_0 = 4\pi^2 c^2 \nu_2^2 M_B \tag{2}$$

Ferrites exhibit extraordinary elastic properties under different strained conditions, and this is what determines how strong they are. It is important to study their elastic properties in the industry. The Debye temperature simplifies the integration of the heat capacity. This temperature indicates the approximate temperature below which quantum effects can occur. Debye temperature (Θ_D) is the maximum temperature a crystal can reach due to its highest normal mode of vibration, which is the highest temperature possible through a single normal vibration. The elastic parameters like average force constant (k_{avg}), lattice constant (a), elastic stiffness constant (C_{ij}), stiffness constant (C_{il}), Young's modulus (Y), Bulk modulus (B), modulus of rigidity (R) are tabulated in **table 2.** The above parameters were calculated using the following equations;

Elastic stiffness constant (Cij);

$$C_{ij} = \frac{k_{avg}}{a} \tag{3}$$

Stiffness constant (Cil),

$$C_{il} = \frac{\sigma \times C_{ij}}{(1-\sigma)} \tag{4}$$

These Poisson's ratio (σ) values were consistent with the theory of isotropic elasticity.Where, magnitude of poisson's ratio, σ=0.3227 is;

Young's modulus (Y),

$$Y = \frac{(C_{ij}-C_{il})\times(C_{ij}+2C_{il})}{(C_{ij}+C_{il})} \tag{5}$$

Bulk modulus (B);

$$B = \frac{1}{3} \times \left(C_{ij} + C_{il}\right) \tag{6}$$

Modulus of rigidity (R)

$$R = \frac{C_{ij}}{3} \tag{7}$$

It was found that all elastic parameters and Debye temperature obtained from FTIR data were in good agreement with reported values[18].

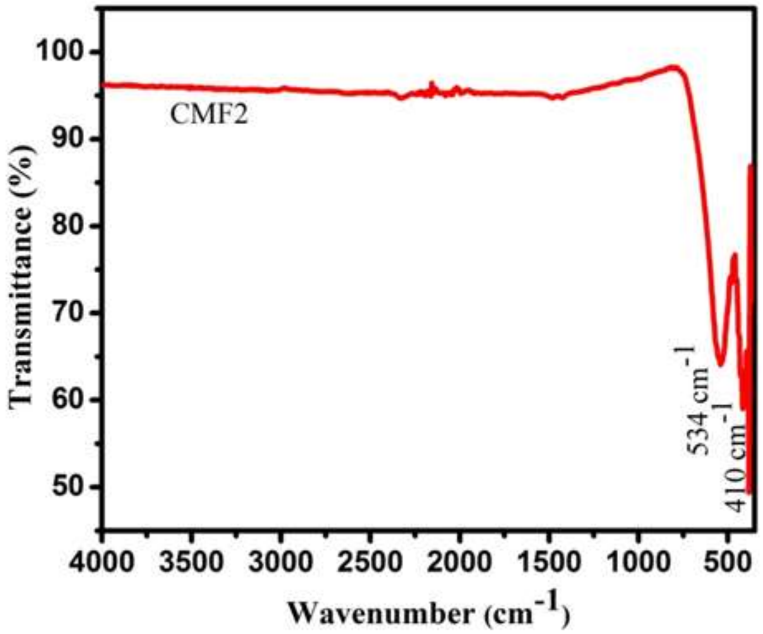

Figure 1FTIR spectra of $Co_{0.75}Mg_{0.25}Fe_2O_4$ nanoparticles

Table 1-Tetrahedral mass (m_A), octahedral mass (m_B), tetrahedral vibrational frequency (ν_1), octahedral vibrational frequency (ν_2), tetrahedral force constant (kt), octahedral force constant (k_o), Debye temperature (Θ_D) of $Co_{0.75}Mg_{0.25}Fe_2O_4$ nanoparticles

x	m_A (amu)	m_B (amu)	ν_1 (cm^{-1})	ν_2 (cm^{-1})	k_t (N/m)	k_o (N/m)	Θ_D (K)
0.25	55.9685	114.6545	534	410	209.51	139.37	679.57

Table 2-Average force constant (k_{avg}), lattice constant (a), elastic stiffness constant (C_{ij}), stiffness constant (C_{il}), Young's modulus (Y), Bulk modulus (B), modulus of rigidity (R)$Co_{0.75}Mg_{0.25}Fe_2O_4$ nanoparticles

x	a (Å)	k_{avg} (N/m)	C_{ij} (GPa)	C_{il} (GPa)	Y (GPa)	B (GPa)	R (GPa)
0.25	8.379	174.4377	208.18	99.19	144.17	102.46	69.39

Conclusions

The magnesium substituted cobalt ferrite nanoparticles synthesized via green method assisted with black pepper (Piper nigrum) aqueous extract as chelating/reducing agents were successfully developed. The higher frequency absorption band at wavenumber ($\nu_2 \approx 534$ cm^{-1}) (ν_1) is caused by scratching vibrations of the tetrahedral metal-oxygen bond and lower frequency absorption band (ν_2) at wavenumber ($\nu_2 \approx 410$ cm-1)is caused by metal-oxygen vibrations in octahedral sites. It was found from all elastic parameters and Debye temperature obtained from FTIR data were in good agreement with reported values. It is our understanding that there are no literature data on the synthesis of Mg substituted $CoFe_2O_4$ via black pepper (Piper nigrum) aqueous extracts.

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