



INFLUENCE OF COBALT IONS SUBSTITUTION ON MICROSTRUCTURE, MAGNETIC AND ACOUSTIC PROPERTIES OF NANOCRYSTALLINE CALCIUM HEXAFERRITES

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Abstract- The series of cobalt ions substituted calcium hexaferrite nanoparticles with composition $\text{Ca}_2\text{Zn}_2\text{Fe}_{12-x}\text{Co}_x\text{O}_{22}$ ($0 \leq x \leq 1$) nanoparticles were synthesized by microwave induced sol-gel combustion method. The influence of cobalt ions substitution on the microstructure, magnetic and acoustic properties of the calcium hexaferrite were investigated by XRD, VSM and ultrasonic pulse technique. The values of lattice parameter a and c is found to be about 5.0418 (Å) and 44.1876 (Å). The lattice parameter a and c increases slightly with increase in substitution of Co^{3+} ions in calcium hexaferrite. From XRD studies, it was observed shows that a single Y-type hexagonal ferrite phase is formed in samples. Vibrating sample magnetometer measurement indicates that the coercivity of the samples of hexaferrite increases with Co^{3+} ions substitution, which is attributed to a increase in crystal anisotropy field by changing the easy-axis of magnetization from c -axis to basal plane. The acoustic studies indicate that the decrease in elastic moduli with Co^{3+} ions concentration strengthened the inter-atomic bonding between various atoms in hexaferrite continuously.

Keywords- Y-type hexagonal ferrite, Nanoparticle, Magnetic properties, Acoustic properties

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Introduction

Nowadays, the need of new magnetic materials explains the considerable interest of researchers on the study of hexagonal ferrites, due to their applications in new emerging technologies. Those technological applications require material with strict control on the microstructure which governs the extrinsic magnetic behavior such as homogeneity, particle size and shape [1]. Hexagonal ferrites especially Y-type ferrites have been proved to be the promising candidates for nanomaterials having above properties by virtue of their ease of applicability in high density recording media, microwave absorption devices, magneto-optic recording media, etc. In order to achieve highly homogeneous particles of cobalt ion substituted hexaferrite, various techniques such as chemical coprecipitation [2], hydrothermal [3], sol-gel [4,5], and glass crystallization [6] have been developed. Conventional solid state method, as the classical ceramic route for preparing hexaferrite, requires high calcinations temperature (1200-1300 °C) which induces sintering and aggregation of particles. Furthermore, the milling process to reduced the particle size from multi domain to single domain, generally yields

non-homogeneous mixture on microscopic scale and results in lattice strain in the materials [7].

The present module of research aims to develop a microwave induced sol-gel combustion, as a novel process which facilitates the production of ultra fine hexagonal ferrite particles especially in nanoscale. It is based on the gelling and subsequent combustion of an aqueous solution containing salts of desired metals and some organic fuel, has been given a voluminous and fluffy product with large surface area [8]. Further attempts are kept under examination to improve microstructure, magnetic properties and acoustic properties of cobalt ion substituted hexaferrite.

Experimental

Sample preparations

The starting materials to synthesized nanostructured hexaferrite samples are AR grade $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, $\text{Zn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, $\text{CO}(\text{NH}_2)_2$ and $\text{Co}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$. The series of cobalt ion PM2 and PM3 having $x=0.2$, $x=0.5$ and $x=0.7$ are selected for this paper. Stoichiometric amount of metal nitrate was dissolved completely in deionized water. The fuel urea was also dissolved in deionized water. Two solutions as prepared were mixed together

to form homogeneous transparent aqueous solution. The solution was then heated to about 100 °C with constant stirring. The aqueous solution of ammonium hydroxide was added to mixed solution and pH of the solution was adjusted to 7. After that, the solution was kept in the digitally controlled microwave oven of 2.45 GHz to evaporate the water and wet gel of high viscosity were obtained. After heating it was then converted into dry gel which in turn burnt completely by evaporating large volume of gases. The ash obtained was grind in agate mortar for about 15 minute and powder obtained are named as PM1, PM2 and PM3.

Characterization

The crystalline structural analysis of the synthesized sample in powder form was performed by a Phillips X’pert Diffractometer and using Cu-Kα radiation source and λ=1.5406 Å with 40 mA 45 KV. The scanning angle range was kept between 10° to 120°. Lattice constants a and c, cell volume (V_{cell}), X ray density (ρ_{x-ray}), bulk density (ρ_m) and porosity (P) of samples PM1, PM2 and PM3 are determined.

The magnetic property of the substituted ferrite was measured with vibrating sample magnetometer (VSM Lakeshore Model No. 665).

The ultrasonic pulse transmission technique [9] was used for the measurement of longitudinal wave velocity (V_l) and shear wave velocity (V_s) at 1MHz. The RF pulse generated by a pulse oscillator was applied to quartz transducer. The acoustic pulse were converted into electrical signals by receiving transducer. The output signal was displayed on a digital taxtronic 2230 oscilloscope. The difference in time(ΔT) between two overlapping received pulse train was noted with the help of timer. The sound velocity was measured using the equation V=L/ΔT where V sound velocity, L length of superconducting specimen, and T time. The accuracy

of the sound velocity measurement was ± 0.5%.

A number of research reports is available in the literature describing various aspects of elastic behavior of different superconducting systems [10-13].

The elastic constants of a material can be determine by measuring the velocity of the longitudinal (V_l) and shear wave (V_s) [14].

The ultrasonic velocities and elastic constants are related as given by the following equations [9].

Longitudinal modulus $L = \rho(V_l)^2$

Rigidity modulus $G = \rho(V_s)^2$

$$B = L - \frac{4}{3}G$$

Bulk modulus

$$\sigma = \frac{3B - 2G}{6B + 2G}$$

Poisson’s ratio

Young’s modulus $E = (1 + \sigma)2G$

The acoustic Debye temperature of materials used to explain the well known solid state problem like lattice vibrations is determined using ultrasonic velocity. The relation is given as

$$\theta = \frac{h}{k_B} \left[\frac{3PN_A}{4\pi V} \right]^{1/3}$$

Where h is the Planck’s constant, k_B Boltzmann constant, N_A Avogadro number, V volume calculated from the effective molecular weight and the density (i.e. M/ρ), P the number of atoms in the molecular formula

and V_m the mean sound velocity defined by the relation

$$V_m = \left[\frac{\frac{2}{V_s^3} + \frac{1}{V_l^3}}{3} \right]^{-1/3}$$

Results and discussion

X-ray diffraction

The diffraction patterns of samples are taken with Phillips X’pert Diffractometer and Cu-Kα radiation with wavelength λ = 1.5406 Å. The XRD pattern of the samples are shown in Fig 1. The crystallographic data are tabulated in Table 1. The data is analyzed by using computer software PCPDF Win, Powder-X and Full proof Suite. By comparing the patterns with JCPDS, the phases in the different samples are determined. The XRD pattern confirms the formation of single phase hexagonal ferrites. Kuhikar [15] reported the values of ‘a’ and ‘c’ as 5.884 Å and 43.938 Å for Ca₂Co₂Fe₁₁LaO₂₂ sample.

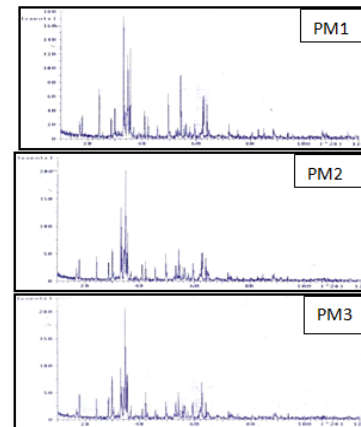


Fig.1- X-ray diffraction spectra of PM1, PM2 and PM3 samples.

Other parameters such as lattice constants (a & c), cell volume (V), X-ray density (ρ_{x-ray}) and bulk density (ρ_m) are enumerated in Table 1. The lattice parameter ‘a’ and ‘c’ and ‘V’ slightly increases with substitution of Co³⁺ ion in calcium hexaferrite sample. This is due to relatively large ionic radius of Co³⁺ (0.67 Å) comparing to that of Fe³⁺ (0.64 Å) for six fold coordination. As a result, the cell volume of the samples of hexaferrite increases after being doped with Co⁺³ ions. The X-ray densities and bulk densities of the substituted hexaferrites also decreases with the increase in the concentration of substituent as reported in Table 1. The enhancement in X-ray density and bulk densities on substitution of Co³⁺ ion in hexaferrite samples is due to the larger molar masses of the substituted samples. The X-ray density is higher than the bulk density (ρ_m) which indicates the presence of pores in the synthesized samples. The porosity increases with increase in the Co³⁺ ions content. The results agree well to that reported by M. B Solunke [16].

Acoustic studies

The values of ultrasonic wave velocity and Debye characteristic

temperature of the synthesized samples are summarized in Tables 2. Table 3 depicts the values of longitudinal modulus, bulk modulus, Young's modulus, rigidity modulus and Poisson's Ratio with Co content (x). It can be seen from the Table 4 that, the longitudinal modulus, bulk modulus, Young's modulus and rigidity modulus decreases with increase in Co³⁺ ions concentration (x) following Wooster's work [19], the variation of elastic constant decrease with in Co³⁺ ions concentration for Ca in Ca₂Zn₂Fe_{12-x}Co_xO₂₂ Superconducting system may be interpreted in term of inter-atomic bonding. Thus, it can be inferred from the decrease in elastic modulus with concentration (x) that the inter-atomic bonding between various atoms is being strengthened continuously. The strength of inter-atomic bonding and type of cations are involved in bond formation. Earlier it has been observed that, substitution of small amount of Pb for Bi in Bi-2212 and Bi-2223 systems enhanced superconducting properties but deteriorate the elastic properties [20]. On the other hand when Fe³⁺ ion is replaced by Co³⁺ ions in Ca₂Zn₂Fe_{12-x}Co_xO₂₂ system, it improves the elastic behavior of the system. This finding can be explained on the basis of change in length of inter-atomic bonding. When Fe³⁺ ions with ionic radius (0.64 Å) are replaced by Co³⁺ ion with larger ionic radius (0.67 Å), it increase the bond length and as a result strength of inter-atomic bonding is expected to decrease and in turn elastic moduli values. The observed increase in Debye temperature (θ) (Table 2) with Co³⁺ ions concentration suggested that the lattice vibrations are decrease due to cobalt ions substitutions. The magnitude of elastic constants and Debye temperature are constant with other Bi2212 based superconducting systems [20]. The values of Poisson's ratio are found in the range 0.02-0.10 for all the concentrations. These values lies in the range from -1 to 0.5 which is in conformity with the theory of isotropic elasticity.

Conclusion

The cobalt ions substituted calcium hexaferrite was synthesized by the microwave induced sol-gel combustion method. The XRD data have confirm the formation of Y-type hexaferrites and the a and c values of the sample supports this confirmation. The substitution of Co³⁺ ions in hexaferrite enhances the magnetic parameter such as coercivity of the samples. The acoustic studies have confirmed the influence of Co³⁺ ions in hexaferrite on acoustic parameter.

Table 1- Lattice constants (a) and (c), cell volume (V_{cell}), X-ray density (ρ_{x-ray}), bulk density (ρ_m) and porosity (P) of samples PM1, PM2 and PM3.

| Composition x | Sample | a(Å) | c(Å) | V (Å) ³ | ρ _{x-ray} (g/cm ³) | ρ _m (g/cm ³) | Porosity (%) |
|---------------|--------|--------|---------|--------------------|-----------------------------------------|-------------------------------------|--------------|
| 0 | PM1 | 5.0390 | 44.1072 | 1239.28 | 4.22 | 3.09 | 27.67 |
| 0.2 | PM2 | 5.0446 | 44.2236 | 1245.32 | 4.16 | 3.11 | 25.26 |
| 0.5 | PM3 | 5.0452 | 44.2512 | 1245.11 | 4.15 | 2.78 | 33.11 |

Table 2- Longitudinal Velocity (V_l), Transverse Velocity (V_s), Mean Sound Velocity (V_m), Mass Density (d), V_l/d (Kg⁻¹m⁴s⁻¹), V_s/d (Kg⁻¹m⁴s⁻¹) and Debye Temperature (θ) of the cobalt ion substituted calcium hexaferrite samples.

| x | V _l (m/s) | V _s (m/s) | V _m (m/s) | V _l /d (Kg ⁻¹ m ⁴ s ⁻¹) | V _s /d (Kg ⁻¹ m ⁴ s ⁻¹) | θ (K) |
|-----|----------------------|----------------------|----------------------|----------------------------------------------------------------------|----------------------------------------------------------------------|---------|
| 0.2 | 2400 | 1749 | 1600 | 0.77 | 0.51 | 1405.63 |
| 0.5 | 2500 | 1860 | 1714 | 0.85 | 0.58 | 2222.54 |
| 0.7 | 2617 | 1991 | 1833 | 1.01 | 0.71 | 2623.02 |

Table 3- Longitudinal Modulus (L), Bulk Modulus (B), Rigidity Modulus (G), Young's Modulus (E) and Poisson's Ratio (σ) of the cobalt ion substituted calcium hexaferrite

| x | L (GPa) | B (GPa) | G (GPa) | E (GPa) | σ |
|-----|---------|---------|---------|---------|------|
| 0.2 | 17.90 | 7.30 | 7.95 | 17.49 | 0.10 |
| 0.5 | 18.21 | 6.83 | 8.59 | 18.15 | 0.05 |
| 0.7 | 17.66 | 6.13 | 8.65 | 17.64 | 0.02 |

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