Investigation of Cation Distributions and Temperature-dependent Magnetic Properties of Polycrystalline $CoFe_2O_4$

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Abstract

Phase-pure cobalt ferrite [$CoFe_2O_4$ (CFO)] nanoparticles are prepared by sol-gel autocombustion technique in order to study its structural and magnetic properties. The presence of mixed spinel cubic structure (space group= *Fd-3m*) is confirmed from the Rietveld refinement of X-ray diffraction (XRD) patterns and Raman spectra study. X-ray photoelectron spectrum (XPS) suggest the existence of Co^{+2} and Fe^{+3} ions. Analysis of the magnetic data shows that coercivity, remanence and saturation magnetization decreases with increase in temperature.

Introduction

- Magnetic oxide (AB_2O_4) has attracted much attention because they have multiple applications in many fields of science (medicine, magnetic recordings, etc.).
- Cobalt ferrite [$CoFe_2O_4$] have earned special interest because of its high coercivity, cubic magnetocrystalline anisotropy, moderate saturation magnetization.
- It exhibit ferrimagnetism with high Curie temperature of T_C ~ 790 K (bulk) and crystallizes in cubic spinel structure (*Fd-3m*).
- $(Co_{1-x}Fe_x)_T[Co_xFe_{2-x}]_OO_4$, where *T* and *O* represents tetrahedral and octahedral sites respectively. For inverse spinel structure x=1 and if x=0 it is normal spinel otherwise it is in mixed spinel structure.
- Particle size and distribution of cations has a huge impact on the electric and magnetic properties.

Objectives

Systematic study of cationic distributions through the results of XRD, Raman spectroscopy, XPS and magnetic measurements in order to deduce the conclusive mechanism for the distribution of cations.

Experimental details

$Fe(NO_3)_3.9H_2O$ + $Co(NO_3)_2.6H_2O$ + $C_2H_5NO_2$

↓

Heating with continuous stirring

↓

$CoFe_2O_4$ Xerogel powder

↓ Grinding

$CoFe_2O_4$ Powder

↓

Calcined at 900 ^{0}C

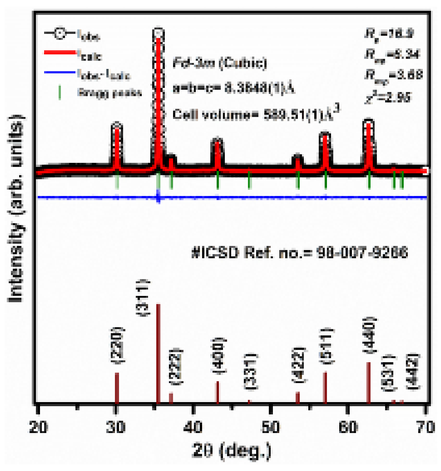
Structural analysis:

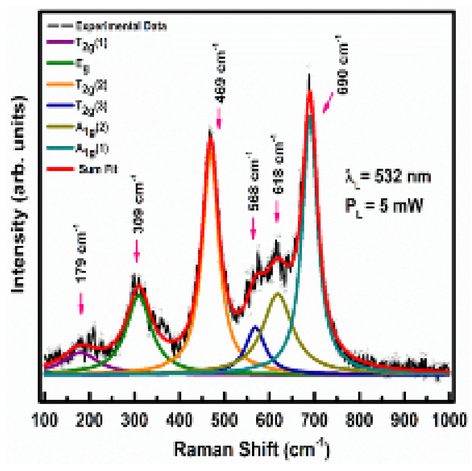
- X-ray diffractometer (Rigaku Ultima IV) using Cu-K_α radiation (λ= 1.5405 Å) with a step size of 0.02^0 at a slow scanning rate of 2^0/min.
- Raman spectra is collected using micro-Raman spectrometer (WITEC ALPHA 300R), with an excitation wavelength of 532 nm and a power of 5 mW.
- X-ray photoelectron spectroscopy (XPS) studies are carried out on a Photo-emission Electron Spectroscopy (PES) beamline (BL-14) of Indus-2 synchrotron source.

Magnetic study:

VSM Lakeshore 7040.

Results and discussions





The crystallite size is calculated from the (311) diffraction peak using Scherrer equation and is found to be 35 nm.

FIGURE 1. Room temperature Rietveld refined XRD patterns (a) and deconvoluted Raman spectrum (b) of CFO confirms the single phase mixed spinel structure.

Inhomogeneous distribution of particles ~50-100 nm in size along with presence of a small amount of pores. EDS spectra confirmed the presence of Co, Fe and O elements.

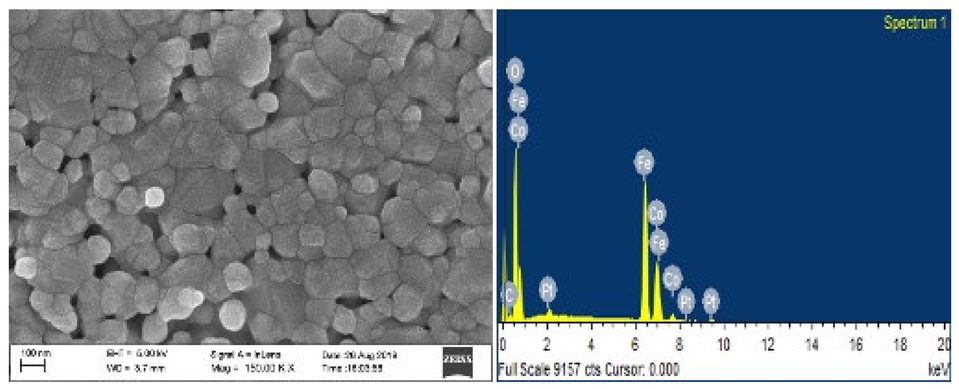
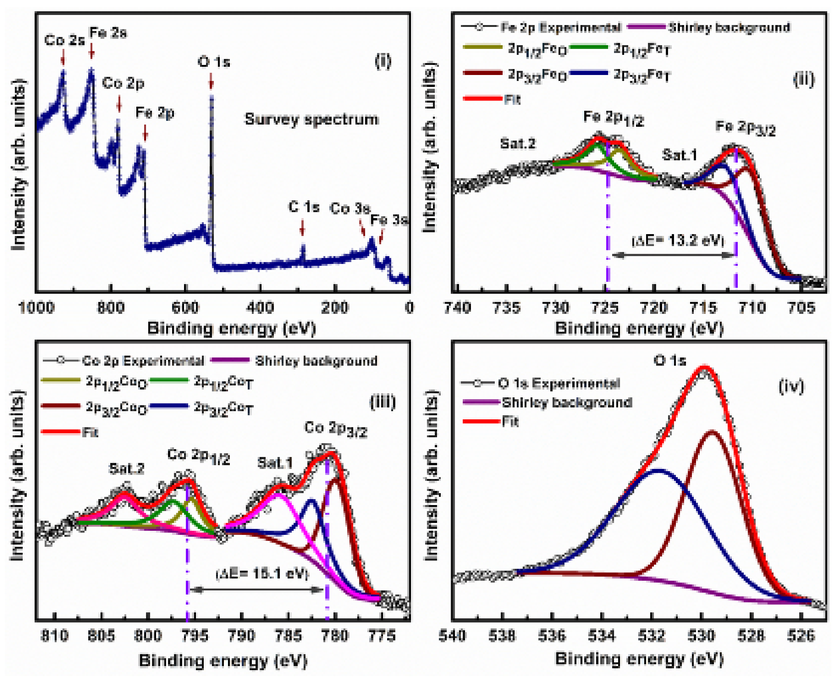
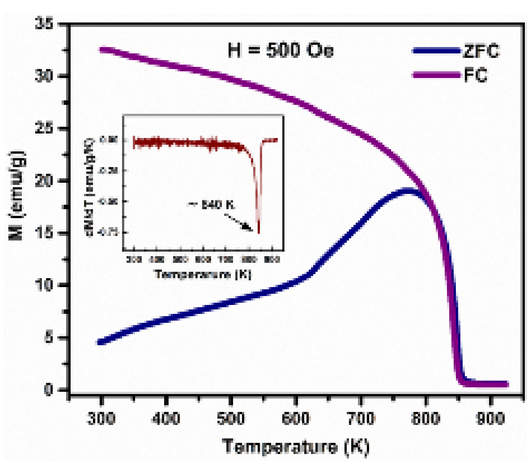


FIGURE. 2. FESEM image and EDS spectra of pure CFO nanoparticles.



The Fe $2p_{3/2}$ and Fe $2p_{1/2}$ are individually deconvoluted into two peaks corresponding to Fe^{+3} at *O* and *T*-sites. Similarly in high resolution XPS spectra for Co 2p, the Peaks that are observed at 779.8 and 782.3 eV are for *O* and *T* –sites Co $2p_{3/2}$ respectively and at 795.3 and 797.2 eV for *O* and *T* – sites Co $2p_{1/2}$.

FIGURE. 3. XPS spectra of CFO measured at room temperature: (i) wide-scan (0-1000 eV), (ii) Fe 2p, (iii) Co 2p and (iv) O 1s.



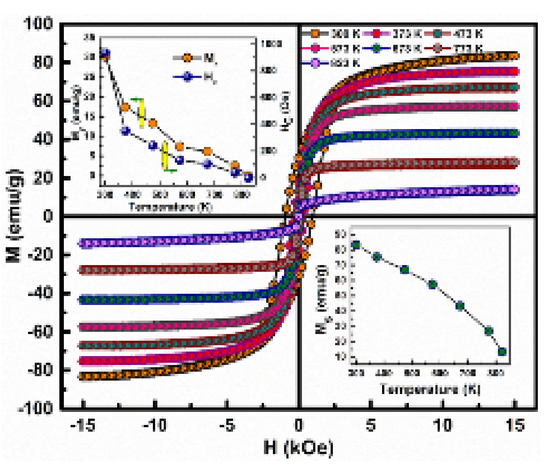


FIGURE 4. (a) Typical M_{ZFC}(T) and M_{FC}(T) curves of CFO measured at 500 Oe. The T_C value is indicated in the first derivative of magnetization $\frac{dM}{dT}$ vs temperature (T). (b) Magnetic field dependence magnetization M(H) measured at various isothermal temperatures. Upper inset shows the dependence of coercive field (H_C) and remanence (M_r) on temperature. Temperature dependence of saturation magnetization (M_S) are shown in lower inset. The solid lines are only guide to eyes.

Conclusions

- The polycrystalline CFO is successfully synthesized by sol-gel auto combustion method.
- Detailed analysis of Rietveld refinement of XRD patterns along with the deconvoluted Raman spectrum confirms the mixed cubic spinel structure of CFO having space group *Fd-3m*.
- XPS results revealed the presence of Co^{+2} and Fe^{+3} ions and are distributed in both tetrahedral and octahedral sites.
- Based on the temperature dependence of magnetic properties study, the Curie temperature is obtained to be ~840 K.

Acknowledgements

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