



Impact of fine particles on the magnetic properties of the $\text{Co}_{1-x}\text{Ca}_x\text{Fe}_2\text{O}_4$

KEYWORDS

Himanshu. L. Padia

Assistant Professor in Physics, Department of Physics, Gujarat Arts & Science College, Ellis-Bridge, Ahmedabad-15, Gujarat, India

ABSTRACT The low field a.c. susceptibility (χ_{ac}) versus temperature, magnetization and Mossbauer effect measurements are reported for the spinel solid solution series $\text{Co}_{1-x}\text{Ca}_x\text{Fe}_2\text{O}_4$ ($x < 0.5$) synthesized by a wet-chemical method before and after high temperature annealing. The observed features for the wet-samples, such as the intense peak χ_{ac} -T curve, the co-existence of paramagnetic doublet and magnetic sextets in Mossbauer spectra, and lower saturation magnetization values confirm fine particle ferrite behavior. Especially, the appearance of the central paramagnetic doublet in Mossbauer spectra and a sharp intense peak in χ_{ac} -T curve in wet samples reveal the presence of super paramagnetic particles induced by fine particle size effects. Further the fine particle nature of wet-ferrite has increased the substitution limit of Ca for Co from 15% (ceramically prepared ferrite) to 30%. The high temperature annealing changes the wet-prepared ferrites into the ordered magnetic structure of ceramic ferrites.

1 Introduction

Wet chemically prepared ferrites normally consist of fine particles and exhibit unusual magnetic properties. This fact has motivated us to synthesize the mixed spinel solid solution series $\text{Co}_{1-x}\text{Ca}_x\text{Fe}_2\text{O}_4$ ($x < 0.5$) consisting of two ferrites $\text{Co}_{1-x}\text{Fe}_2\text{O}_4$ possessing predominantly an inverse spinel structure and cubic symmetry and CaFe_2O_4 nearly normal with orthorhombic symmetry², by Co-precipitation technique (wet chemical method) at lower temperature (55°C) and to examine the effect of non-magnetic Ca^{2+} substitution for Co in CoFe_2O_4 on the magnetic and structural properties. Though this system has been prepared ceramically and studied^{3,5}, no attempt has been made to prepare the same by wet-chemical method. The spinel oxide materials synthesized by two different methods exhibit differences in their magnetic properties^{6,7} has generated a considerable interest in the comparative study of magnetic and structural properties of spinel ferrites such as MgFe_2O_4 [Ref 8], CuFe_2O_4 [Ref 9] and $\text{ZnCo}_{1-x}\text{Fe}_2\text{O}_4$ [Ref 10].

In this paper's report, X-ray diffraction, magnetization, Mossbauer effect and a.c. susceptibility measurements on the mixed spinel solid solution series $\text{Co}_{1-x}\text{Ca}_x\text{Fe}_2\text{O}_4$ ($x < 0.5$) synthesized by wet chemical method. For the sake of comparative study, annealed the wet samples of $\text{Co}_{1-x}\text{Ca}_x\text{Fe}_2\text{O}_4$ at 1000°C and their magnetic properties were studied as well.

2. Experimental

The Co-Ca ferrites with variable composition ($x = 1$ to 0.5) were prepared by air oxidation of an aqueous suspension containing CO_2^+ , Ca^{2+} and Fe^{2+} cations in proper proportions. The starting solutions were prepared by mixing 100 ml of aqueous solutions of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ and $\text{COCl}_2 \cdot 6\text{H}_2\text{O}$ in stoichiometric proportions. A 2M solution of NaOH was prepared as a precipitant. The starting solution was added into the precipitant. The suspension ($\text{pH} = 9$) containing dark green intermediate precipitates was formed. Then the suspension was heated and kept at the temperature of 55°C while air was bubbled uniformly into the suspension to stir it and to promote oxidation reaction, until all the intermediate precipitates changed into

the dark brownish precipitates of the spinel ferrite. The samples were filtered, washed and dried at room temperature for 24 hours.

The wet samples of Co-Ca ferrites were annealed in air at 1000°C for 24 hours. After high temperature annealing the wet samples exhibit weight loss (around 2-1%) because of the removal of water and the hydroxyl ions even after the drying process.

The X-ray powder patterns were recorded using FeK α radiation on phillips diffractometer. The saturation magnetization of each sample was measured using the high field hysteresis loop technique¹¹. The low field a.c. susceptibility measurements on powdered samples were carried out in the temperature range 300 K to 800 K using double coil set up¹² operating at a frequency of 263 Hz and r.m.s field of 0.5 Oe. The Mossbauer spectra were obtained in the constant acceleration mode at 300 K transmission geometry.

Result and Discussion

For all samples of the system, the X-ray diffraction pattern showed sharp lines in the range of $2\theta = 10^\circ$ to 90° , corresponding to single phase (fcc) for $x \leq 0.3$ (wet) and $x \leq 0.2$ (annealed wet, AW) and a mixture of two phases (fcc and orthorhombic) for wet ($x = 0.3$ to 0.5) and AW ($x = 0.2$ to 0.4) samples, respectively. The diffraction lines were slightly broad for wet samples due to particle size effect, whereas they were sharp for, the AW samples. The observed single phase (fcc) behaviour for wet samples up to $x = 0.3$ suggests that almost 30% of calcium has been substituted for cobalt compared with 15% for the ceramically prepared samples.^{3,4} The average particle size estimated from full width of half maximum of the diffraction line arc 200 Å and 550 Å for wet and AW samples, respectively, and the particle size of both wet and AW samples remain nearly constant for all Ca-concentrations. The particle size of AW samples are nearly three times larger than the wet samples. This indicates that the high temperature annealing of wet samples has increased the crystallite size up to the order of ceramic ferrite.

The values of saturation magnetization per formula unit, n_B , at 77 K and 300 K, for wet and AW samples are shown in Fig. 1 (a) and (b) respectively. n_B value at 300 K and 77 K show no variation with x for wet samples Fig. 1 (a) on the other hand n_B values for AW samples at 77 K and 300 K initially increase up to $x = 0.2$ and then decrease with increasing x from $x = 0.2$ to 0.3 (Fig. 1 b) This is consistent with the n_B behaviour reported for ceramically prepared Co—Ca ferrite series.^{3,4} The smaller n_B values of wet samples compared with AW samples (Fig 1) may be attributed to the random distribution of particle spins and line particle size effect, The plots of normalized susceptibility $\chi T/\chi_{RT} = \chi_{ac}$ against temperature for $x \leq 0.5$ depicted in Fig. 2 and 3 exhibit interesting features namely (i) a presence of a peak in χ_{ac} -T curve and (ii) differences in the shape of the χ_{ac} -T curves. A sharp peak observed in χ_{ac} -T curve of wet sample is nearly two times more intense compared to the AW samples of the same Ca-concentration (x) due to the fine particle effect confirming the presence of superparamagnetic panicles. All these features can be understood on the basis of the domain state aspect or these materials.

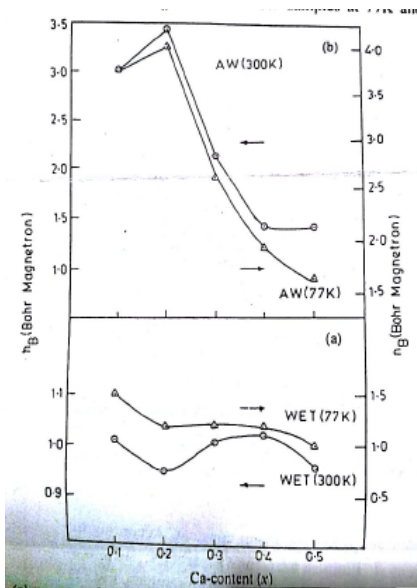


Fig. 1 (a) n_B versus ca-content (x) for wet Co-Ca ferrites at 77 K and 200 K (b) n_B versus x for AW Co-Ca ferrites at 77 K and 300 K

The observed peak in χ_{ac} -T curve for AW samples may be attributed to single domain to superparamagnetic (SD—SP) transition. It has been suggested, that if there are SP particles in the material than they would behave as SD particle below the blocking temperature (T_b). T_b depends on the individual cluster volume V and is given by

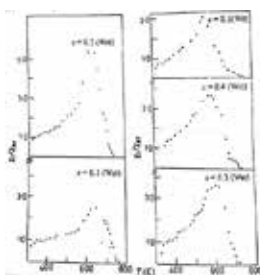


Fig. 2 Normalized susceptibility (χ_T/χ_{RT}) versus temperature for wet Co-Ca ferrite samples for $x < 0.5$

$$VJ_s H_c = 2K T_b$$

Where J_s is the saturation intensity and K is the Boltzmann constant. According to Bean¹³ H_c is large for SD, whereas it is almost zero for SP particles. Therefore χ , which is inversely proportional to H_c is large for SP (wet samples. Fig. 2) than SD (AW samples, Fig 3).

The Curie temperature (T_c) determined from the a.c. susceptibility measurements are displayed in Fig. 4 for both wet and AW samples. T_c for wet samples decreases with increasing x up to $x \leq 0.3$ because antiferromagnetic substitution of CaFe₂O₄ reduces T_c and thereafter it displays increase with Ca content for $x > 0.3$ indicating phase separation of the ferriimagnetic, type (Fig 4). A similar trend has been observed for T_c of AW samples which displays decrease in T_c up to $x = 0.2$ and thereafter it increases. Results are in good agreement with ceramically prepared samples,^{3,4} which also show decrease in T_c up to $x = 0.15$ indicating that the system remains in single phase (fcc) up to $x = 0.15$.

This suggests that wet chemical preparation technique has unable us to substitute Ca for Co in Col-xCaxFe₂O₄ up to $x = 0.3$ because of fine particle size effect.

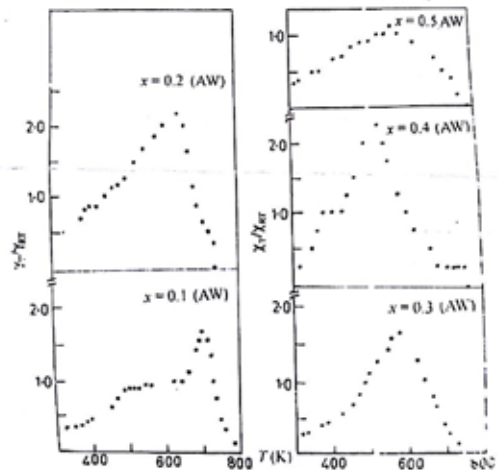


Fig. 3 Normalized susceptibility (χ_T/χ_{RT}) versus temperature for AW Co-Ca ferrite for $x < 0.5$

Typical room temperature (300 K) Mossbauer spectrum for $x = 0.1$ wet sample shown in Fig. 5 is characterized by the simultaneous presence of a central paramagnetic doublet and a magnetically split component. On the other hand, the Mossbauer spectrum of $x = 0.1$ ceramically prepared samples³ exhibits two well defined Zeeman patterns. The appearance of the central paramagnetic doublet in the Mossbauer spectrum of $X = 0.1$ wet-sample agrees with its lower value of n_B compared to $x = 0.1$ AW samples (Fig 1) and can be attributed to the presence of superparamagnetic particles induced by the line particle size effects.

The observed differences in the structural and magnetic properties of wet and AW samples are attributed to the fine particle size effect and non-magnetic Ca²⁺ substitution for Co²⁺. The high temperature annealing changes the wet prepared ferrites into the ordered magnetic structure of ceramic ferrite.

Conclusion

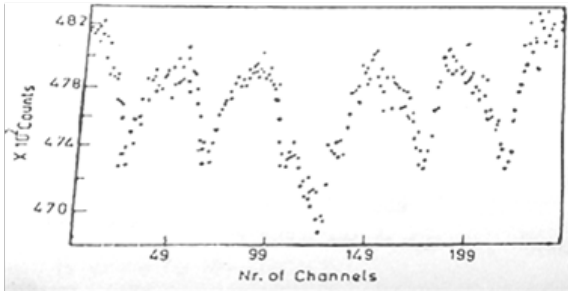


Fig. 5 Room temperature Mossbauer spectrum for $x=1$ wet Co-Ca sample

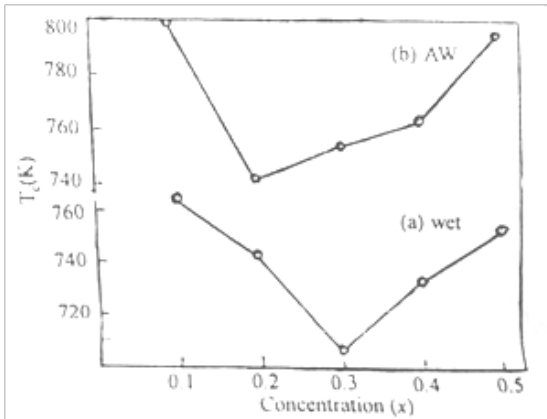


Fig. 4 Variation of TC with x for Co-Ca samples (a) wet. (b) AW

Fine particles play an important role in controlling the magnetic properties of the ferrites has been shown by the present study. It is established that the wet chemical prepared mixed spinel series $\text{Co}_{1-x}\text{Ca}_x\text{Fe}_2\text{O}_4$ contain fine particles of the order of 200 \AA which give rise to the unusual magnetic properties to the system like superparamagnetism leading to the suppression of long range magnetic ordering and quenching of magnetic moments inspite of having Curie temperature greater than 700 K . It is found that wet preparation technique has enabled to substitute Ca for Co up to 30%, where as the Ca substitution limit for Co in ceramic samples is only up to 15% [Ref 3, 4]. The high temperature annealing of the wet prepared ferrites transforms them in to the ordered magnetic structure of ceramic ferrites having long range ferri magnetic ordering.

REFERENCE

- Sawatzky G. A., Van der Woude F & Morrish A. M. J. Appl Phys. 39 (1969) 1204. | 2. (1957) 332. | 3. Upadhyay R. V. Baldha G. J. & Kulkarni R. G. J. Magn. Mater. 61 (1986) 109. | 4. G. Mat Res Bull. 21 (1986) 1051. | 5. Baldha G. J., Upadhyay R. V. & Kulkarni R. G. J. Mat Sci. 23 (1988) 3357. | 6. Magn. Mater., 7 (1978) 52. | 7. Petreru M. Gennaro A. & Borriesci N. J. Mater. Sci., 17 (1982) 429. | 8. Chem., 64 (1986) 141. | 9. Pandya P. B., Joshi H. H. & Kulkarni R. G. J. Mater Sci. Letts, 10 (1990) 474. | 10. Pandya P. B., Joshi H. H. & Kulkarni R. G. J. Mater Sci. 26 (1991) 5509. | 11. Likhite S.D., Radhakrishnamurthy C. & Shahashtrabudhe P.W. Rev. Scin. Instr. 36 (1965) 1558. | 12. S.D. & Shahashtrabudhe P.W., Proc. Indian Acad. Sci. 87a (1978) 245 | 13. Bean C.P. J. Appl. Phys. 26 (1955) 1381 | Decker B. F. & Kasper J. S. Acta Cryst. 10 Baldha G. J., Upadhyay R. V. & Kulkarni R. Borriesci N., Garbassi F. & Pizzinij S. J. Kulkarni R. G. & Joshi H.H. J. Solid State