

Comparative study of structural and magnetic properties of Cobalt, Lithium and Tin Ferrite

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ABSTRACT

We have prepared nano particles of Cobalt Ferrite CoFe_2O_4 , Lithium Ferrite LiFe_5O_8 and Tin Ferrite SnFe_2O_4 with the help of citrate precursor method. Selection of lithium ferrite was done in order to detect any difference in properties due to different size. Their structural and magnetic properties were studied with the help of X-Ray diffractometer and vibrating sample magnetometer. All the samples were annealed at high temperature (450°C – 650°C), to reduce the chances of obtaining superparamagnetism. On increasing the temperature sharp rise in particle size of Tin ferrite was seen but in lithium ferrite and Tin ferrite, this was not significant. In the context of magnetic properties, the saturation magnetization was observed to be nearly constant with temperature in case of tin and lithium ferrite. The coercivity of Tin and Lithium ferrite was nearly independent of temperature but in cobalt ferrite there was sharp decrease in coercivity with temperature. We expect that present work will help in synthesis of ferrites by a low cost route making analysis of properties easier.

I. INTRODUCTION

For many years, it has been known that magnetic nanoparticles with small size can be considered having single domain and they display properties markedly different from the bulk.¹ One of their interesting properties is the presence of magnetic relaxation process that is due to the thermal effect and existence of energy barriers separating the local minima for different equilibrium states of system. So, the magnetic behaviour of a small particles depends on its relaxation time $\tau = \tau_0 \exp\left[\frac{KV}{K_B T}\right]$, where τ_0 is about 10^{-10} s and weakly depending on temperature, K_B is Boltzmann constant, T is temperature, K and V are anisotropy and average volume². At very small particle size the anisotropy factor is not sufficient to stop the magnetization vector from switching to a lower energy state.

Another interesting feature of nanoparticles is the due to surface spin disorder which is induced by broken exchange bonds at the surface. As a result, the system should be considered as a core shell structure with ferromagnetically aligned core spins and a spin glass like surface layer, whose thickness can vary¹.

II. MATERIALS AND METHOD

For synthesizing Cobalt ferrite, Cobalt nitrate $\text{Co}(\text{NO}_3)_2$ and Ferric Nitrate $\text{Fe}(\text{NO}_3)_3$ were taken separately in stoichiometric proportion and dissolved in minimal amount of distilled water. In case of Lithium ferrite, we took lithium Nitrate and in case of Tin ferrite, SnCl_2 was taken in place of Cobalt nitrate. This solution was mixed with citric acid solution and was heated for two hours with constant stirring at 68°C . The resulting brown jelly like substance was placed in oven for 24 hours at temperature 80°C and became fluffy like bricks. This was sintered at two temperatures 450°C and 650°C . XRD and VSM measurements for these samples were carried out.

III. RESULTS AND DISCUSSIONS

The X-Ray diffraction analysis was done and crystallite size was calculated by Scherrer's formula^{13, 14}. At the same time, the measurements of saturation magnetization, coercivity etc. was done by vibrating sample magnetometer and overall, shown in table 1.

We can see that although the particle size has increased but the percentage rise is very small in lithium ferrite and it is very large in Tin ferrite with temperature¹. This trend is in agreement with LD Tung et. al. It has also been found that the annealing temperature affects the particle size significantly⁴. The fig 1 is a comparative view of XRD plots, showing peaks approximately at same locations in all samples. We can say that molecular formula of Lithium ferrite is giving it somewhat other structure, but it is Tin ferrite, whose crystallite size changed much.

None of the samples were found to have superparamagnetism because the selected temperature range was high and particles size was large (40 to 90 nm). Tin ferrite is seen exhibiting large change in particle size with rise of temperature. (fig 2)

The following graphs (figure 3 and figure 4) show the VSM plots obtained by us at 450° and 650°C temperatures.

In very first sight, we can see that in all, the area of the graph has decreased when the temperature was raised. The Tin ferrite graph has very small area, indicating that it is better material for the applications where cyclic magnetization process is being done. On the other side its coercivity and retentivity seems very less as compared to others.

Saturation magnetization of Lithium Ferrite (29.5 to 27.3 emu/g) and Tin ferrite (2.3 to 1.76 emu/g) has very small change in comparison to cobalt ferrite (36.7 to 41.4 emu/g). (figure 5).

There is possibility that lithium ferrite and tin ferrite samples have canted spins at the surface. With increasing size, due to increasing temperature, the thickness of shell having canted spin might have increased in proportion, the result being reduced saturation magnetization^{5,6}. This study can be extended further with the help of Mössbauer spectra in which shift in peaks may assure about existence of core shell model^{3, 4}.

The wohlfarth model assumes that there is a uniform magnetization throughout the particle and it remains so throughout the rotation process¹⁰. Generally the energies required to reverse the spin orientation within single domain are larger than those needed in bigger ones so coercivity is larger in small particles. In other word, when

particle size decreases to single domain, the domain rotation is preferred, consuming more strength of external field making coercivity high. At the blocking temperature, when thermal energy is sufficient to break the anisotropy barrier, the coercivity gets zero. Below this temperature, the coercivity is the field which together with thermal energy can overcome the anisotropy. Therefore coercivity increases with size, below blocking temperature¹⁰. (Figure 6)

In our samples, we easily conclude that in case of lithium ferrite (171.9 to 134.7 G) and Tin ferrite (186.8 to 171.6 G), there is no significant increase in coercivity with temperature and say particle size. It can be attributed to core shell structure of them already discussed above¹⁰. In all the samples, the coercivity is more at lower temperature which verified the established theories about dependence of coercivity with temperature¹¹.

Retentivity of cobalt ferrite was seen to decrease with temperature (19.5 to 16.8 G). The increasing temperature causes vigorous vibrations of magnetization vector and memory of earlier magnetization is erased. Sample of Tin ferrite also demonstrated fall in retentivity (0.54 to 0.3 G) but lithium ferrite shows rise in retentivity (7.69 to 8.3 G) with temperature. (Figure 7)

This anomaly can be attributed if we assume varying thickness of shell having canted spins surrounding the core. In Lithium ferrite the enhancement in thickness of canted spin surface layers may have screened the inner core from external changes. The increasing fraction of atoms having canted spin can also lead to this anomaly.

After plotting the graphs, it could be seen that in Tin ferrite the change in particle size with temperature is maximum, but saturation magnetization, coercivity and retentivity changed minimally with temperature. On the other hand, Cobalt and Lithium Ferrite show little change in particles sizes, but there magnetic properties change substantially, although in opposite manner. This trend may a coincidence but should be studied further.

The purity of samples was also analyzed with ICDD database available to us. The sample CoFe_2O_4 at 450°C was found containing traces of FeO in some amount, but Fe_3O_4 was not found. Low intensity peaks at 33.162, 35.630 and 49.465 degrees indicate presence of very small amount of Fe_3O_4 in this. At higher temperature these impurities are almost absent. Tin Ferrite sample was also free from SnO, FeO, Fe_3O_4 etc, but had some Fe_2O_3 at 450°C as some lines indicating its presence are seen.

IV. CONCLUSION

We can conclude that lithium and tin ferrite have completely different trends in magnetic and structural and magnetic properties and their potential as the future smart materials is yet to be explored. In all the cases, we have found that phases were almost clear, but impurities were seen less in fraction at higher temperature. All the samples were sufficiently good, but contained less impurities at high temperature. This may be due to thermal breaking of oxides of them. Perhaps higher temperature of production is most suited for these ferrites.

This type of materials needs further investigation in order to isolate trends in properties, so that they may be used to synthesize the materials with controlled properties in future¹².

REFERENCES

- [1.] L. D. Tung, V. Kolesnichenko, G. Caruntu, D. Caruntu, Y. Remond, V. O. Golub, C.J. O'Connor, L. Spinu, Annealing effect on the magnetic properties of nanocrystalline zinc ferrite, *physica B*, 319(2002)116-121.
- [2.] Eun Jung Choi et. al, Superparamagnetic relaxation in CoFe_2O_4 nanoparticles, *Journal of magnetism and magnetic materials*, 262(2003), L198-202
- [3.] R N Panda et.al, Magnetic properties of nanocrystalline Gd or Pr substituted CoFe_2O_4 synthesized by citrate precursor technique
- [4.] 4. Adriana S. Albuquerque, Jose' D. Ardisson, Waldemar A.A. Macedo, Nanosized powders of NiZn ferrite: Synthesis, structure and magnetism, *Jour. Appl. Phys.* Vol. 87 p4352- 4357 (2000)
- [5.] 5. T. Sato, K. Haneda, M. Seki, T. Tijima, *Appl. Phys. A* 50 (1990) 13.
- [6.] 6. Caizer and M. Stefanescu, magnetic characterization of Ni-Zn ferrite powder prepared by the glyoxylate precursor technique, *J. Phys. D: Appl. Phys.*, 35(2002) 3035-3040.
- [7.] 7. Georgia C. Papaefthymiou, Nanoparticle magnetism, *Nano Today*, 2009. 4, 438-447
- [8.] 8. M Rajendran, R. C. Pullar, A. K. Bhattarcharya, D. Das, S. N. Chintalapudi, C. K. Majumdar, Magnetic properties of nanocrystalline CoFe_2O_4 powders prepared at room temperature: variation with crystallite size, *Journal of Magnetism and Magnetic Materials*, 232, (2001)
- [9.] 9. Chao Liu, Adam J. Rondinone, Z. John Zhang, Synthesis of magnetic spinel Ferrite CoFe_2O_4 nanoparticles from ferric salt and characterization of the size dependent superparamagnetic properties, *Pure Appl. Chem.* , Vol 72, Nos. 1-2, pp. 37-45, 2000
- [10.] 10. Georgia C. Papaefthymiou, Nanoparticle magnetism, *Nano Today*, 2009. 4, 438-447
- [11.] 11. Chao Liu, Adam J. Rondinone, Z. John Zhang, Synthesis of magnetic spinel Ferrite CoFe_2O_4 nanoparticles from ferric salt and characterization of the size dependent superparamagnetic properties, *Pure Appl. Chem.* , Vol 72, Nos. 1-2, pp. 37-45, 2000
- [12.] 12. A. K. Bandopadhyay, *Nanomaterials*, New age international publishers
- [13.] 13. P. Scherrer, *Gottinger Nachrichten Gessel*, Vol. 2, 1918, P 98
- [14.] 14. Patterson, A. 1939, "The Scherrer's formula for X Ray particle size determination", *Phys. Rev.* 56(10), 978-982, doi:10.1103/physRev.56.978

Table 1. The table of data obtained

Sample 450 ^o C	Crystallite size (nm)	Saturation Magnetization Emu/g	Coercivity (G)	Retentivity (G)
CoFe ₂ O ₄	43.4	36.7	1460.0	19.5
SnFe ₂ O ₄	45.0	2.3	186.8	0.54
LiFe ₅ O ₈	89.6	29.5	171.9	7.69
650^oC				
CoFe ₂ O ₄	46.5	41.4	654.1	16.8
SnFe ₂ O ₄	89.6	1.76	171.6	0.3
LiFe ₅ O ₈	92.7	27.3	134.7	8.3

Figure 1. XRD plots of samples (comparative view)

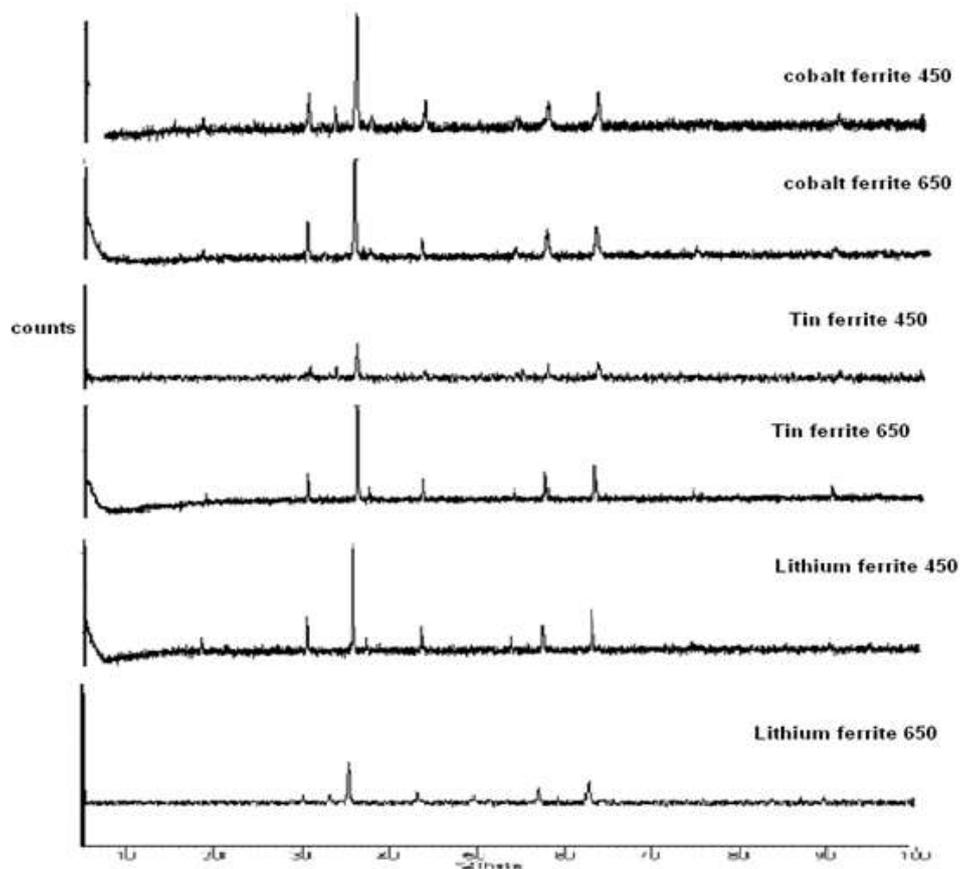


Figure 2 Particles sizes at 450°C and 650°C

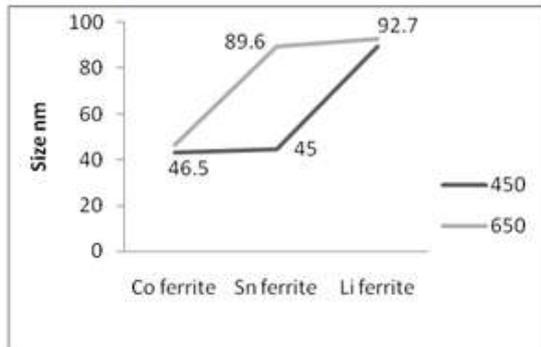


Figure 3 VSM plots of samples at 450°C

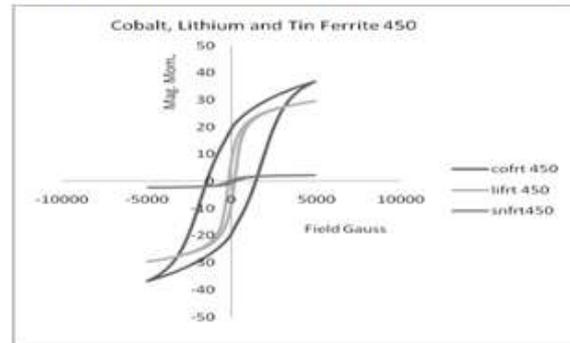


Figure 4 VSM Plots of samples at 650°C

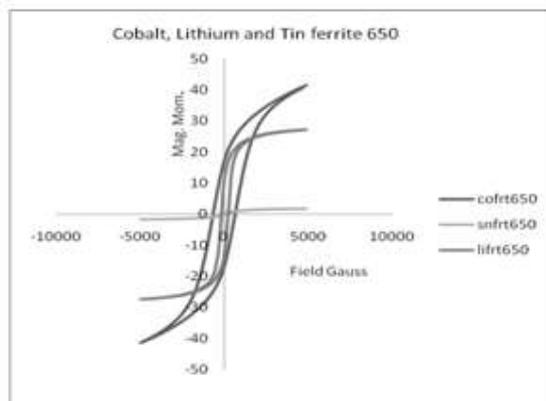


Figure 5 Saturation magnetization of samples

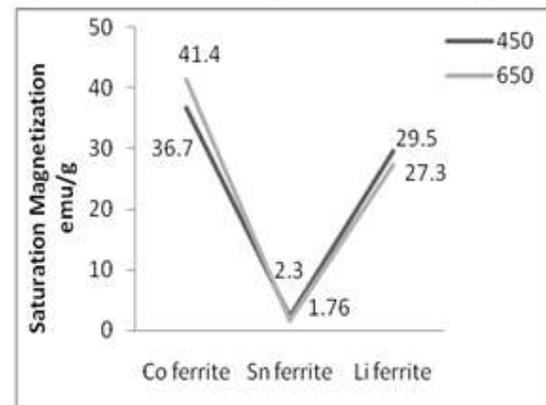


Figure 6 Coercivity of samples

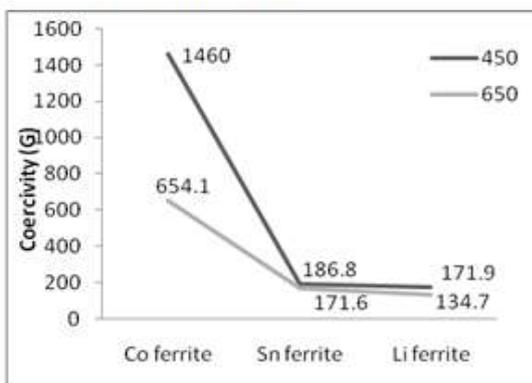


Figure 7 Retentivity of samples

