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Tailoring of the Magnetic and Structural Properties of Nanosized Ferrites

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Abstract

Spinel ferrites are porous ceramics with remarkable electrical and magnetic properties. They belong to a technologically important class of magnetic materials which have high resistivity and chemical stability. These properties make them suitable for a wide variety of applications, where other magnetic materials cannot be used. Magnetic, electric, and structural properties of ferrites are tunable. These are currently of great research interest due to the ease of tailoring their magnetic properties by systematic substitution of cations and by proper choice of preparation techniques and post preparation treatments. The Cr^{3+} cations have a strong preference to occupy in the B-site and have an affinity for anti-ferromagnetic coupling with Fe ions. Thus, partial or total substitution of one of the cations with Cr^{3+} induces magnetic frustrations in the spinel ferrite system, which leads to interesting magnetic properties. Therefore, it is very interesting to study variation in magnetic properties on replacement of Cr in the place of Fe in spinel ferrites. This chapter explains tailoring of magnetic and structural properties of some spinel ferrites via solution-self-combustion, fuel-to-oxidizer ratio substitution, and proper substitution.

Keywords: spinel ferrite, chromites, solution-self-combustion, X-ray diffraction, DC magnetization studies

1. Introduction

Spinel ferrites are porous magnetic ceramics. Ferrite nanoparticles have extensive scope in the fundamental and applied research area. They have tunable electrical and magnetic properties that have wide practical applications. Recently, much attention has been paid on the magnetic oxide nanoparticles because they have wide range of applications such as magnetic storage media, gas sensors, ferrofluid technology, semiconductors, batteries, solar energy

transformation, heterogeneous catalysis, magnetocaloric refrigeration, and medical diagnosis [1]. Nanoparticles are much more active than larger bulk particles because of their higher surface area, and they display unique physical and chemical properties [2]. Spinel oxides have general formula $D\text{Fe}_2\text{O}_4$, where D is a divalent cation like Co, Ni, Zn, Mn, Mg, Cu, etc. Spinel oxides can be prepared by various techniques such as forced hydrolysis, microwave synthesis, sol-gel method, co-precipitation, polyol, self-combustion reaction, and sonochemical [3–7] methods. Among these methods, the self-combustion method, particularly solution self-combustion, is one easy method through which highly pure crystalline and homogenous material can be prepared with high yield [8]. In solution self-combustion method, it is easy to control the stoichiometry and crystallite size, through preparation conditions and post treatments, which have an important direct influence on the magnetic properties of the ferrite.

In solution self-combustion, there are two components, nitrate and fuel. The fuel helps in the combustion of nitrates. The powder characteristics such as crystallite size, surface area, and size distribution are governed by enthalpy or flame temperature generated during combustion which itself depends on the nature of the fuel and fuel-to-oxidizer ratio [9]. There are number of different fuels active in self-combustion such as glycine, citric acid, tartaric acid, urea, etc. Among these fuels, citric acid is a good one to initiate combustion reaction due to its negative combustion heat, -2.76 kcal/g [10].

The Cr^{3+} cations have strong preference to occupy in the B-site and have an affinity for anti-ferromagnetic coupling with Fe ions. The partial or total substitution of one of the Fe^{3+} cations with Cr^{3+} cations induces magnetic frustrations in the spinel ferrite system, which leads to interesting magnetic properties. Therefore, it is very interesting to study variation in magnetic properties on doping of chromium ion in the place of Fe ion in spinel system [11].

Highly pure and identical nanoparticles are essential for excellent performance of the materials. By tuning of structural and magnetic properties, we can have highly pure and identical nanoparticles with exact physical and chemical properties suitable for particular application. In application level, large-scale synthesis at low cost is needed. With these aims, this work presents low cost synthesis of highly pure nanospinel ferrites via solution self-combustion technique, and the tuning of structural and magnetic properties is undertaken in terms of fuel-to-nitrate ratio and Cr doping. This synthesizing process neither requires sophisticated instruments nor a high sintering temperature.

2. Experimental

Nanosized NiCrFeO_4 , CoCrFeO_4 , and ZnCrFeO_4 fuel lean, stoichiometric and fuel rich samples, and fuel rich $\text{CoCr}_x\text{Fe}_{2-x}\text{O}_4$ (with $x = 0, 0.2, 0.4, 0.6, 0.8$ and 1.0) were prepared by solution self-combustion technique using analytical grade corresponding to high purity metal nitrates (Merck-Germany) and citric acid ($\text{C}_6\text{H}_8\text{O}_7\text{H}_2\text{O}$) as oxidizing agents and fuel, respectively. The ratio of citric acid to metal nitrate (F/N ratio) was taken as 0.65 for fuel lean sample, 1 for stoichiometric sample, and 1.35 for fuel rich samples. The solutions of three nitrates (Fe, Cr, Co/Ni/Zn) and citric acid were prepared separately, mixed, and stirred completely to form a

homogenous solution using magnetic stirrer. The homogenous solution was evaporated on a magnetic hot plate. On evaporation, solution gets thickened to a thick gel. The temperature was then increased to 200°C to start the auto-ignition process, which resulted in the formation of a fluffy residue [12–16]. It was powdered and used for further studies.

The X-ray diffraction spectrum of the samples was taken by an X-ray diffractometer (Rigaku MiniFlex) with Cu-K_α radiation. The X-ray diffraction (XRD) patterns of all the samples were fitted with MAUD Rietveld refinement program. DC magnetization measurements were obtained using vibrating sample magnetometer (VSM- Lake Shore 7304) with a maximum applied field of 10 kOe [16].

3. Tuning via fuel-to-oxidizer ratio

XRD spectra of all CoCrFeO₄, NiCrFeO₄, and ZnCrFeO₄ samples are shown in **Figures 1–3**, respectively. Well-defined characteristic reflections in powder X-ray diffraction patterns clearly indicate the formation of the spinel structure. XRD pattern of all the stoichiometric and fuel rich samples shows that they have single-phased cubic spinel structure, whereas fuel lean samples show a small percentage of impurity phases, α-Ni in fuel lean NiCrFeO₄, α-Co in fuel lean CoCrFeO₄, and α-Fe₂O₃ in ZnCrFeO₄. Average crystallite sizes (D) for the samples are calculated by substituting the FWHM values of the maximum intensity (311) peaks in the Scherrer formula:

$$\text{Crystallite sizes (D)} = \frac{0.9\lambda}{\beta \cos \theta} \quad (1)$$

where λ is the wavelength of X-rays and β is the width of the most intense peak in the XRD after correction for instrumental broadening. Actual density (ρ) of the samples is determined

Figure 1. Powder XRD of CoCrFeO₄ samples with Rietveld fitting, reprinted from Sijo [15], with permission from Elsevier.

Figure 2. Powder XRD of NiCrFeO₄ samples with Rietveld fitting, reprinted from Sijo [15], with permission from Elsevier.

using Archimedes principle. Porosity of the samples is calculated from the actual and x-ray densities. Crystallite size (D), density (ρ), and porosity of all samples are given in **Table 1**.

It is seen from **Table 1** that the crystallite size of fuel lean sample is many times greater than that of the stoichiometric samples and fuel rich samples. Presence of the impurity phase creates lattice

Figure 3. Powder XRD of ZnCrFeO₄ samples with Rietveld fitting [14].

Sample name	F/N ratio (ϕ)	Crystallite size (nm) (± 1)	Density (gm/cm ³)	Porosity (%)	M _R (emu/g) (± 0.1)	M _S (emu/g) (± 0.1)	H _C (Oe) (± 1)
CoCrFeO ₄	0.65	29.5	4.0	22	5.9	28.5	352
CoCrFeO ₄	1;1	3.4	4.6	12	0.3	4.8	580
CoCrFeO ₄	1.35;1	5.7	4.7	10	0.5	5.5	645
NiCrFeO ₄	0.65	30.1	2.8	46	6.4	27.8	182
NiCrFeO ₄	1;1	3.2	3.6	32	0.25	2.3	192
NiCrFeO ₄	1.35;1	5.7	4.1	23	0.6	5.5	118
ZnCrFeO ₄	0.65	15	2.3	57	0.05	1.43	51
ZnCrFeO ₄	1;1	5	3.4	35	0.02	0.83	49
ZnCrFeO ₄	1.35;1	6	4.2	23	0.001	0.73	16

Source: Sijo [15] and Sijo et al. [14].

Table 1. Structural and magnetic parameters for the influence of fuel-to-nitrate ratio.

defects in the form of vacancies in the spinel ferrite phase and leads to an expansion of the lattice, which in turn makes the material porous and increases the crystallite size. In fuel lean samples, the amount of fuel is not adequate enough to react completely with metal nitrates and to release enough heat to form well-developed nanosized grains. Since the combustion reaction is incomplete, impurity phases of α -Ni, α -Co and α -Fe₂O₃ are also formed along with the spinel phase in samples prepared under the fuel lean condition. From these results, it is clear that stoichiometric fuel-to-oxidizer ratio results finest single-phased nanoparticles [14–17].

The variation of crystallite size with fuel content is plotted in **Figure 4**. From the figure, it is clear that the finest particles are obtained for stoichiometric fuel-to-nitrate ratio, and there is a small increase of crystallite size in the sample prepared under the fuel rich condition.

Figure 4. Crystallite size with fuel-to-nitrate ratio: modified from Sijo [15] and Sijo et al. [14].

Figure 5. Room temperature magnetization curve of CoCrFeO₄ samples.

Smaller crystallite sizes of samples prepared under stoichiometric ratio may be due to the fact that more gaseous products are formed under this condition, leading to the breaking up of particles on escaping and resulting in finer particles. The superior powder properties present in CoCrFeO₄, ZnCrFeO₄, and NiCrFeO₄ samples prepared on stoichiometric ratio is due to the dominant effect of the number of gas molecules over the flame temperature [14–17].

Room temperature (RT) M-H loops of CoCrFeO₄, NiCrFeO₄, and ZnCrFeO₄ samples are shown in **Figures 5–7**, respectively. The coercivity and remanence are obtained directly from the M-H loops. Some of the samples show nonsaturating behavior, and hence, the value of saturation

Figure 6. RT magnetization curve of NiCrFeO₄ samples. **Figures 5 and 6** are reprinted from Sijo [15], with permission from Elsevier.

Figure 7. Room temperature magnetization curve of ZnCrFeO_4 samples [14].

magnetization of these samples is estimated by plotting M vs. $1/H$ for $1/H$ tending to zero. All the DC magnetization parameters are listed in **Table 1**. As seen from structural characterization using Rietveld fitted XRD, the CoCrFeO_4 , NiCrFeO_4 , and ZnCrFeO_4 samples prepared at fuel lean condition have the presence of a small amount of impurity phases $\alpha\text{-Co}$, $\alpha\text{-Ni}$, and $\alpha\text{-Fe}_2\text{O}_3$, respectively. The higher magnetic moments observed in these samples can be attributed to the presence of impurity phases. The saturation magnetization depends on the average crystallite size. As the size increases, the saturation magnetization is also increased. From **Table 1**, we can conclude that the behavior of saturation magnetization (M_s), coercivity (H_c), and remanence (M_r) are highly dependent upon the fuel-to-nitrate ratio, and we can tune the structural and magnetic properties of spinel ferrites by changing fuel-to-oxidizer ratio.

4. Tuning via Cr^{3+} substitution

We can tune the structural and magnetic properties of spinel ferrites by suitable substitution also. For this, consider the samples $\text{CoCr}_x\text{Fe}_{2-x}\text{O}_4$ (with $x = 0, 0.2, 0.4, 0.6, 0.8$ and 1.0). The combined X-ray diffraction spectra for Cr doped powder are shown in the **Figure 8(a)**. These diffraction spectra provide clear evidence of the formation of ferrite spinel phase in all the samples. The broad XRD line indicates that the ferrite particles are of nanosize. The crystallite size for each composition was calculated from Rietveld fitting of spectra and given in **Table 2**. Room temperature magnetization measurements are taken for all samples and shown in **Figure 8(b)**. The magnetic parameters of all the samples are obtained and tabulated in **Table 2**, the value of remanence and coercivity obtained directly from individual M-H loops, while saturation magnetization obtained by plotting $1/H$ vs. M and extrapolating to zero.

From **Table 2**, the crystallite size, remanence, saturation magnetization, and coercivity were plotted vs. Cr content of $\text{CoCr}_x\text{Fe}_{2-x}\text{O}_4$ samples and are shown in **Figure 9**. From this figure, we

Figure 8. X-ray diffractograms (a) and RT magnetization curves (b) of Cr-doped powder samples. Reprinted from Sijo [13], with permission from Elsevier.

can clearly observe that crystallite size, remanence, saturation magnetization, and coercivity decreases, as chromium content increases. The area of hysteresis curve linearly decreases with increase in Cr content. That is, CoFe_2O_4 has the largest area, and CoCrFeO_4 has the smallest area inside the hysteresis loop. This indicates that the increased Cr substitution has made the material magnetically soft [14–17].

5. Conclusion

High-purity magnetic spinel ferrites can easily prepare by solution self-combustion method. It provides energy and cost-saving advantages over other methods. The finest nanoparticles obtained for stoichiometric fuel-to-nitrate ratio in solution self-combustion method. Increased Cr substitution in ferrites has made the material magnetically soft. That is, the structural and magnetic properties of ferrites are function fuel content and doping content, and therefore, they are highly tuneable via selection of proper preparation method, proper fuel content,

Sample name	Crystallite size (nm) (±1)	M_R (emu/g)(±0.1)	M_s (emu/g) (±0.1)	H_C (Oe) (±1)
$\text{CoCr}_{0.0}\text{Fe}_{2.0}\text{O}_4$	21	17.9	50.8	1080
$\text{CoCr}_{0.2}\text{Fe}_{1.8}\text{O}_4$	12	5.7	35.8	377
$\text{CoCr}_{0.4}\text{Fe}_{1.6}\text{O}_4$	11	1.9	25.3	192
$\text{CoCr}_{0.6}\text{Fe}_{1.4}\text{O}_4$	09	2.1	16.9	291
$\text{CoCr}_{0.8}\text{Fe}_{1.2}\text{O}_4$	07	1.1	14.6	227
$\text{CoCr}_{1.0}\text{Fe}_{1.0}\text{O}_4$	05	0.4	2.6	378

Table 2. Structural and magnetic parameters of $\text{CoCr}_x\text{Fe}_{2-x}\text{O}_4$ samples [13].

Figure 9. Crystallite size, remanence, saturation magnetization and coercivity vs. Cr content of $\text{CoCr}_x\text{Fe}_{2-x}\text{O}_4$ powder samples. Reprinted from Sijo [13], with permission from Elsevier.

and via proper substitution. Therefore, we can desirably modify properties of spinel ferrites according to the requirement and can use in wide range of applications.

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