

The synthesis and the magnetic properties of Co-Ti Fe₂O₄ ferrite doped with rare earth ions Nanoparticles

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Abstract: Co_{1+x}Ti_xR_yFe_{2-2x-y}O₄ (with x =0.1 & y= 0.02) , (R= Gd, Ho, Er, Nd and Ce) were prepared employing the standard double sintering ceramic technique. The powder was subjected to X-ray diffraction to demonstrate that spinel structure with small secondary phases were obtained due to the doping with rare earth. The physical properties were influenced by rare earth doping substitution. The preparation of nanoparticles less than 50 nm was confirmed by transmission electron microscope (TEM). The samples were more characterized by IR absorption spectroscopy. Vibrating sample magnetometer was employed to probe the magnetic properties of the samples. It was found that rare earth doping enhances the magnetic properties.

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1. Introduction

Magnetic spinel ferrite nanoparticles are of interest in examining the relation-ships between magnetic properties and crystal structure. Spinel ferrites have been investigated in recent years for their useful electrical and magnetic properties and applications in information storage systems, magnetic cores, and medical diagnostics. Co- Ti ferrites is a well known promising candidate for switching and memory device applications. Recently, several series of substituted Co-Ti ferrite composites covering a wide range of properties have become commercially available.

Rare earth (R) elements possess large magnetic moments, large magneto crystalline anisotropy and very large magnetostriction at low temperatures due to the localized nature of 4f electrons [1,2]. Rare earth-iron based compounds (RFe₂) are known to exhibit very large magnetostriction and these compounds are employed as active elements in several magnetostrictive transducers. However, the large conductivity of these compounds limits the usage of the transducers to low frequencies (few kHz).

It was reported that Partial substitution of rare earth[3] cations in Co–Ti ferrites lattice (which occupy the regular positions on the tetrahedral or octahedral sites), cause structural distortion and induce strains in the material due to the contribution from the large single ion anisotropy from the rare earth sublattice and the microstructure and magnetic properties of Co-Ti ferrites would change significantly[4,5]. In this paper, the effects of different rare earth addition (Er, Ho, Nd, Ce) on the microstructure and magnetic properties of Co-Ti ferrites are discussed.

2. Experimental procedure

The ferrites with general formula Co_{1+x}Ti_xR_yFe_{2-2x-y}O₄ (with x =0.1 & y= 0.02) were prepared using the standard double sintering ceramic technique. The starting materials were high purity oxides of Fe₂O₃, CoO, TiO₂ and R₂O₃ (R= Gd, Ho, Er, Nd and Ce) as produced by the British Drug House (BDH). Firstly, the rare earth oxide powders were dried at 700°C for 24 hours to prevent any environmental humidity. Then the hot powder of rare earth oxide was added to the mixture of the other oxides with stoichiometric ratios according to formula. Following on from this the mixture was carefully grinded manually for up to 3 hours, then this was transferred to agate ball mill for another two hours. After that, the mixture was pressed into pellet forms using uniaxial press with a pressure of 1.9 x 10⁸ N/ m². Pre-sintering was carried out at 600 °C with a heating rate of 4°C/m for 10 hours. The samples were grinded again and pressed for another sintering process at 900 °C for 10 hours with a heating rate of 4 °C/m. Again the samples were grinded and pressed and the final sintering was performed at 1150 °C for 5 hours. All samples were cooled to room temperature with the same rate of heating. Some of the samples were crushed again in an agate mortar to obtain fine powder for the magnetic susceptibility measurements, X-ray and IR analysis. The two surfaces of the other pellets were polished to obtain a uniform thickness and coated with silver paste (BDH) as a good Ohmic contact surface.

Phase purity and composition were checked by X-ray diffraction, using CuKα radiation of wavelength 1.5418 Å at 35 kV and 30 mA. (2θ = 15^o to 80^o) at room temperature. The IR absorption spectra of the samples were recorded using an FTIR double-beam spectrophotometer (model Cary 5E) in the wavelength range of 400 to 4000 cm⁻¹. Transmission Electron Microscopy (TEM) analysis was performed by JEOL

JEM2010F and vibrating sample magnetometer (VSM) was used to investigate the magnetic properties at room temperature.

3. Results and Discussion

Structural and Morphological Analysis

The XRD spectrum of the $\text{Co}_{1+x}\text{Ti}_x\text{R}_y\text{Fe}_{2-2x-y}\text{O}_4$ (with $x=0.1$ & $y=0.02$), ($\text{R}=\text{Gd}, \text{Ho}, \text{Er}, \text{Nd}$ and Ce) nanocrystallites is shown in Fig. 1. The XRD analysis reveal the formation of spinel structure in all samples for the different rare earth addition with the appearance of small peaks representing secondary phases, showing well defined reflection of allowed planes. The addition of the rare earth ions to the system acts as a sintering catalyst that helps in the development of the solid solution at lower temperatures [6]. The most important parameters affect the role of rare earth addition are the ionic radii and the electronic configuration. The larger radii prevent rare earth [7].

$$a = d_{hkl} \sqrt{h^2 + k^2 + l^2}$$

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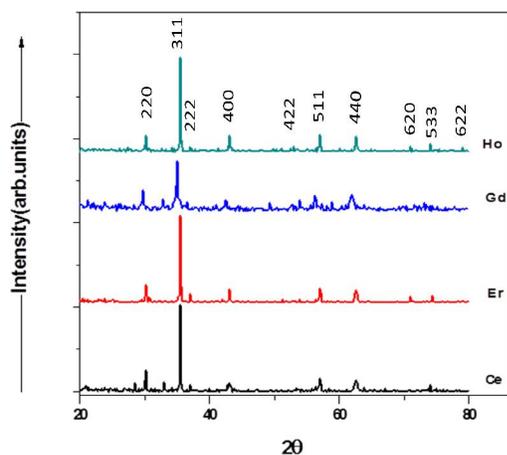
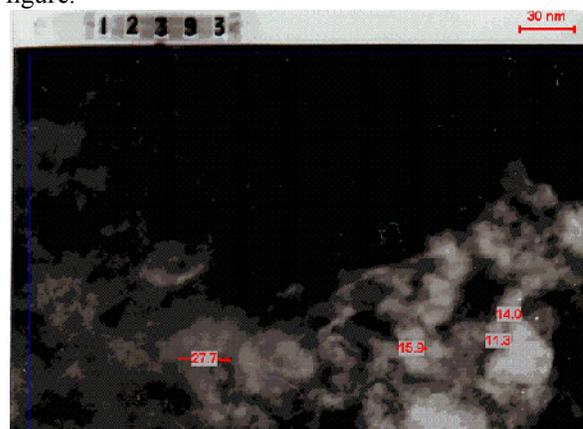


Figure 1. X-ray diffraction pattern for the $\text{Co}_{1+x}\text{Ti}_x\text{R}_y\text{Fe}_{2-2x-y}\text{O}_4$, $y=0.02$, $x=0.1$, ($\text{R}=\text{Ce}, \text{Er}, \text{Ho}, \text{and Nd}$)

Table 1. X-ray density

Rare earth element	Lattice parameter (a) Å	X-ray density D_x (gm/cc)
Ho	8.37399	5.3346
Er	8.38192	5.3321
Ce	8.38384	5.3155
Nd	8.38435	5.3160
Gd	8.92237	5.3070

To evaluate the morphology of the prepared powder, high resolution images of Transmission Electron Microscopy were taken and shown in Fig. 2(a, b) for the prepared samples doped with Er and Nd, respectively. It was determined that the average crystallite size to be ~ 11 to 27 nm. As they are magnetic ferrite crystallites, the particles are agglomerated and composed of nanocrystallites held together by magnetic interaction[8] as illustrated in the figure.



(b)

Figure 2 (a): TEM image of the doped Er sample and (b) TEM image of the Doped sample with Nd powder

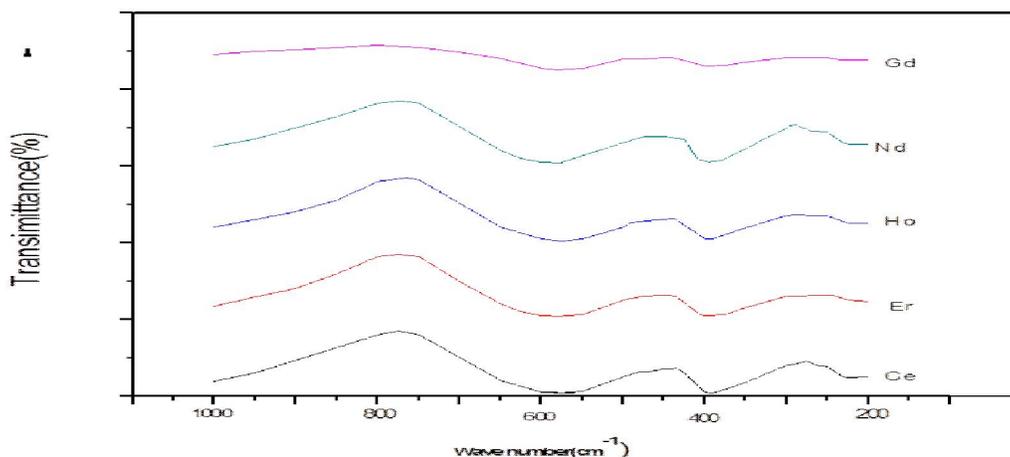


Figure 3. Infrared (IR) for the samples $\text{Co}_{1+x}\text{Ti}_x\text{R}_y\text{Fe}_{2-2x-y}\text{O}_4$ (with $x=0.1$ & $y=0.02$), ($\text{R}=\text{Gd}, \text{Ho}, \text{Er}, \text{Nd}$ and Ce)

The IR transmission spectra of the samples $\text{Co}_{1+x}\text{Ti}_x\text{R}_y\text{Fe}_{2-2x-y}\text{O}_4$ (with $x=0.1$ & $y=0.02$), ($\text{R}=\text{Gd}, \text{Ho}, \text{Er}, \text{Nd}$ and Ce) is illustrated in Figure 3 and reported in Table 2 as a function of rare earth content. There are four bands characterizing ferrites which can easily be observed in the range $200-700\text{ cm}^{-1}$. The difference in positions of the bands for the various composition was expected because of the difference in the distances for the octahedral and tetrahedral ions. We can see that, ν_1 is assigned to the vibrational band of the Fe^{3+} ions existing in tetrahedral (A) position. The variation of ν_1 with the rare earth types is attributed to the difference of their ionic radii as well as the calculated lattice constant (a) (see Table 1). The vibrational frequency band ν_2 is assigned to the vibrational frequencies of Fe^{3+} with oxygen anion in the B site. The vibration frequency band ν_3 is assigned to the vibrational frequency due to the presence of divalent metal ions with oxygen in the octahedral position. The lattice vibrational frequency ν_4 occurs in the spinel matrix.

Table 2. IR transmission of the samples $\text{Co}_{1+x}\text{Ti}_x\text{R}_y\text{Fe}_{2-2x-y}\text{O}_4$ (with $x=0.1$ & $y=0.02$), ($\text{R}=\text{Gd}, \text{Ho}, \text{Er}, \text{Nd}$ and Ce)

Element	ν (cm^{-1})			
Ce	580	475	395	260
Ho	578	470	390	268
Er	573	473	345	260
Nd	580	480	397	280

Magnetic properties of the compounds $\text{Co}_{1+x}\text{Ti}_x\text{R}_y\text{Fe}_{2-2x-y}\text{O}_4$; $x=0.1, Y=0.02, \text{R}_y=\text{Gd}, \text{Ce}, \text{Ho}, \text{Er}$ and Nd are listed in Table 3 and are plotted in Figure 4. It

can be seen from the results that all magnetic parameters are enhanced by the rare earth doping. It can also be noted that when the Fe ions are substituted by rare earth ions at lattice sites, the rare earth ion interactions are stronger than Fe-Fe interactions. Generally speaking, the magnetic moments of iron and heavy rare earth atoms are anti-parallel in heavy rare earth (Er, Ho, and Gd) [9].

Table 3. Magnetic parameters of the samples $\text{Co}_{1+x}\text{Ti}_x\text{R}_y\text{Fe}_{2-2x-y}\text{O}_4$ (with $x=0.1$ & $y=0.02$), ($\text{R}=\text{Gd}, \text{Ho}, \text{Er}, \text{Nd}$ and Ce)

Rare earth element	Hc(Oe)	Mr(Oe)	Ms (Oe)	Mr/Ms
Nd	448.3	22.14	69.24	0.319
Ce	377.5	15.76	60.92	0.258
Ho	419.3	17.51	64.12	0.273
Er	474	19.37	64.85	0.298

The sudden increase of the magnetization at high fields, due to the magnetic interaction between rare earth ions and Co^{3+} ions, is a dynamical phenomenon which depends on the sweep rate of the applied field as found in other magnetic systems [10,11]. Paramagnetic moments of the heavy rare earth tri-hydrides (Er, Gd, and Ho) are smaller than the pure elements and paramagnetic moments of the light rare earth tri-hydrides (Ce, Nd) are higher than for pure elements [12]. It allows to conclude that the value of magnetic moment depends on antiferromagnetic coupling

between the spins of 4f electrons and the magnetic moment of s and d electrons. When s and d electrons are localized they are correlated with 4f electrons and "screen" magnetic moment.

The substitution (Er,Nd) s and d-electrons are localized and the moment is anomalously small because of such screening 4f moments and non-magnetic behavior of Ti sublattice.

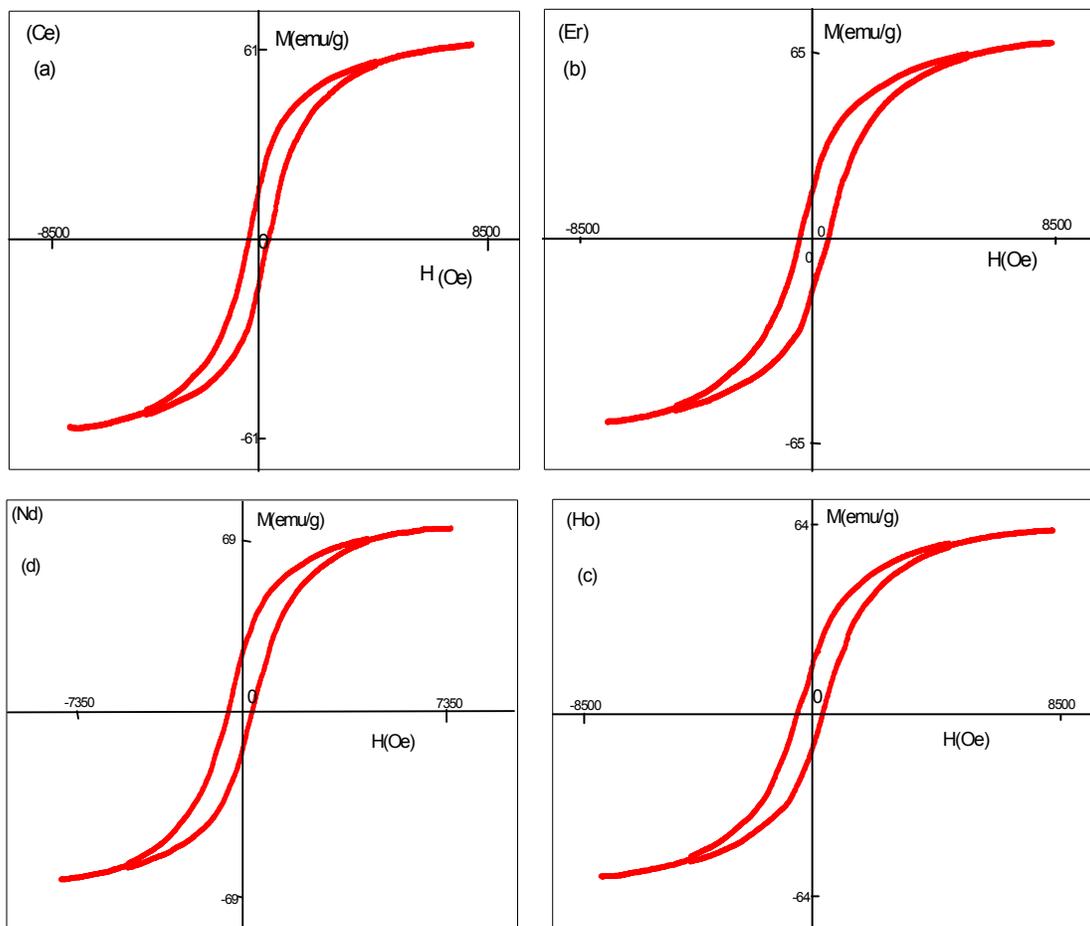


Figure 4. Magnetic hysteresis loops for $\text{Co}_{1+x}\text{Ti}_x\text{R}_y\text{Fe}_{2-2x-y}\text{O}_4$ (with $x=0.1$ & $y=0.02$), (a) Ce, (b) Er, (c) Ho, and (d) for Nd.

Conclusion

This work reports on the synthesis of $\text{Co}_{1+x}\text{Ti}_x\text{R}_y\text{Fe}_{2-2x-y}\text{O}_4$ (with $x=0.1$ & $y=0.02$), (R= Gd, Ho, Er, Nd and Ce) using standard double sintering ceramic technique. XRD of samples revealed that the substitution of rare earth elements for Fe in Co-Ti ferrites mainly produces secondary phases. Structural parameters such as lattice parameter, and crystallite size were affected by the substitution. The hysteresis loop study shows enhancement in the magnetic properties due to the substitutions by different rare earth elements.

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References

- [1] Yang Ying-chang, Kong Lin-shu, Sun Shu-he, Gu Dongmei(1988):Intrinsic magnetic properties of SmTiFe_{10} J. Appl. Phys., 63: 3702.
- [2] Li Hong-shuo, Hu Bo-ping, Coey J.M.D. (1988):

- Spin reorientation transitions in Dy(Fe₁₁Ti). *Solid State Commun.*, 66: 133.
- [3] Fuxiang Cheng, Chunsheng Liao, Junfeng Kuang, Zhigang Xu, Chunhua Yan, Liangyao Chen, Haibin Zhao, and Zhu Liu (1999): Nanostructure magneto-optical thin films of rare earth (RE=Gd,Tb,Dy) doped cobalt spinel by sol-gel synthesis, *J. Appl. Phys.*, 85:2782-2784.
- [4] Rezlescu N, E Rezlescu (1993): The influence of Fe substitutions by R ions in a Ni-Zn Ferrite. *Solid State Communications*, **88**:139-141.
- [5] Rezlescu N, E. Rezlescu, C. Pasnicu and M. L. Craus (1994): Effects of the rare-earth ions on some properties of a nickel-zinc ferrite. *J. Phys.: Condens. Matter*, 6: 5707-5716.
- [6] Rezlescu N., L. Rezlescu, P.D. Popa (2000): Influence of additives on the properties of a Ni-Zn ferrite with low Curie point. *J. Magn. Magn. Mater.*, 194: 215-216.
- [7] Vasiliu A., Gh. Maxim, M.L. Craus (1972): Some magnetic properties and the phase equilibrium of the compounds in the Ca_xNi_{1-x}Fe₂O₄ system. *Phys. Stat. Sol. A*, 13: 371.
- [8] William E. Lee and W. Mark Rainforth (1994): *Ceramic Microstructure*, 1st ed., CHAPMAN & HALL, London, 1994, pp. 457-496.
- [9] Wang K.-Y., D.-X. Chen, J. Arcas, M. Multigner, P. Crespo, M. Vazquez, A. Hernando (1997): Formation and magnetic properties of compounds Er(Fe_{1-x}Co_x)_{11.35}Nb_{0.65} (0 ≤ x ≤ 0.4). *Journal of Alloys and Compounds*, 252: L32-L34
- [10] Hardy V., S. Majumdar, S.J. Crowe, M.R. Lees, D.McK. Paul, L. Herve, A. Maignan, S. Hebert, C. Martin, C. Yaicle, M. Hervieu, B. Raveau (2004): Field induced magnetization steps in intermetallic compounds and manganese oxides. *Phys. Rev.*, B 69: 020407(R).
- [11] Kuberkar D.S., M.B. Stone, P. Schiffer, S.K. Malik (2005): Sharp step-like metamagnetic transition in the charge-ordered manganite compound (La_{0.3}Eu_{0.2})(Ca_{0.3}Sr_{0.2})MnO₃. *J. Phys. Condens. Matter.*, 17: 989.
- [12] Wallace, W. E. (1978). Magnetic properties of metallic and inter-metallic hydrides, in: *Hydrogen in Metals 1*, Chapter 7, (ed. I. G. Alefeld and J. Volkl), Springer Berlin, 1978.

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