

A Review on 1+ and 4+ cations doping in cobalt ferrites for their potential applications

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ABSTRACT

In recent years, researchers are working on enhancing various properties of ferrite materials because of their versatile field of technological applications such as electronics, communications, automation, sensors, energy etc. Ferrites can be categorized structurally as spinel, garnet, magneto plumbites, and orthoferrites. Which, a spinel ferrite is one of the most important polycrystalline oxides which has more industrially viable applications. The cations doping in the spinel ferrites play a vital role to control electrical and magnetic properties. Hence, these properties can be modified for the ferrite system with suitable dopants. In this collective review, the projection of different properties of cobalt ferrite (CaFe_2O_4) such as magnetic and electric properties are discussed. As well as the possible impact of simultaneous doping of materials such as lithium (Li^+) and titanium (Ti^{4+}) are covered. It is found that by doping the lithium and titanium in a cobalt ferrite system, an entirely new set of properties can be obtained. As lithium is the lightest cation and titanium is the high-corrosion-resistance cation, they can enhance various physical properties in the doped spinel oxides.

Keywords: Cobalt Ferrite, Cations Distribution, Magnetic Properties, Dielectric Properties.

Introduction

Ferrites are made up of many small crystals, which are rigid, fragile, iron-containing and mostly magnetic at room temperature. They are low cost and have good corrosion resistance also. Ferrites can be classified into three types: spinel, hexagonal and garnet ferrites [1]. Amongst these spinel ferrites can be used as switches, transducers, actuators, etc. [2]. Cobalt is a ferromagnetic metal with a specific curie temperature. By the transition temperature its structure transits between HCP and FCC structure. Hence, the combination of cobalt and iron, specifically ferrites, has been known as a chemically stable and strong magnetic material for a long time. When suitable compounds are added to a cobalt ferrite, its structural properties can be changed. By doping Ti and Li in the spinel ferrite, electrical and magnetic properties can be modified [3, 4]. Ti-doped Cobalt ferrite is having very less conductivity, while with the doping of Li and the thermal treatment, the said spinel ferrite electric conductive might be enhanced [5, 6].

Electric and Magnetic Properties of Cobalt Ferrite Nanoparticles:

Muzquiz – Ramos et. al. has observed that for CoFe_2O_4 the M_s , M_r and H_c increase up to certain temperatures. After the critical point of temperature M_s exponentially increased while M_r and H_c substantially decreased [7]. Torres et. al. observed that for CoFe_2O_4 , in the temperature range, of 5 K to 280 K the value of H_c and M_s decreased drastically, and superparamagnetic behaviour is exhibited [8]. Kanagesan et. al. and Mauricio A. Medina et. al. also find that CoFe_2O_4 behaves as superparamagnetic materials at room temperature with low H_c value [9, 10]. Maaz et. al. has seen similar results for H_c at different temperatures in that the value of H_c decreases from 15000 Oe to 750-980 Oe when the temperature is increased from 77 K to 300 K [11]. Ajroudi et. al. has observed that the CoFe_2O_4 behaves as an N-type semiconductor and its conductivity increase at high temperature but by increasing the amount of Co in the ferrite system it becomes stable [12]. Khandekar et. al. observed the n-type semiconducting behaviour of CoFe_2O_4 at room temperature and resistivity decreases and dielectric constant increases with the increase in calcination temperature [13]. Hossain et. al. obtained CoFe_2O_4 using the sol-gel method and observed soft ferrimagnetic behaviour as well as a dielectric constant that has higher values at low frequencies and decreases at high frequencies [14]. Razia Nongjai et. al. displayed similar results that at high temperatures CoFe_2O_4 shows high conductivity which decreases at high frequencies [15]. Veena Gopalan et. al. measured the dielectric permittivity of CoFe_2O_4 which is inversely proportional to the frequency but remains constant at very high frequencies [16]. Krutika L. Routray et. al. synthesized CoFe_2O_4 using three different methods namely solid-state reaction, co-precipitation and auto-combustion method and observed that CoFe_2O_4 shows ferrimagnetic nature and dielectric parameters have similar behaviour [17]. A few of the results related to the magnetic properties of doped CoFe_2O_4 systems are tabulated as follows:

Table 1 Comparison of magnetic properties of CoFe_2O_4 at different temperatures

Temperature	M_s (emu/g)	M_r (emu/g)	H_c (Oe)	Reference
5 K	77 - 80	-	14000 - 17100	[8]
77 K	40.8	34.4	11000 - 15000	[11]
280 K	62 -71	-	8.3 - 264	[8]
300 K	68	31.7	750 - 1205	[11]
573 K	41	12	643	[7]
873 K	47	16	891	[7]
1173 K	68	5	103	[7]
1573 K	85	4	99	[7]

Effect of Ti Doping in CoFe₂O₄

Patil and Kotake (2018) synthesized $\text{Co}_{1+x}\text{Ti}_x\text{Fe}_{2-2x}\text{O}_4$ and the magnetic measurements showed that by increasing the amount of Ti in the Co site, the values of M_s , M_r and H_c decreases rapidly [18]. Similarly, Vaithyanathan et. al. (2015) show that the magnetic parameters decreased due to a smaller fraction of Ti in CoFe_2O_4 spinel ferrites [19]. In the contradictory, Amaliya et. al. (2018) synthesized $\text{Co}_{1-x}\text{Ti}_x\text{Fe}_2\text{O}_4$ by the sol-gel method and observed from magnetic measurement results that by increasing the amount of Ti in A – site rather than B the values of M_s , M_r and H_c increase rapidly [20]. Pal et. al. (2018) showed different results from what is discussed above i.e. M_r decreases with increases in Ti while M_s increases up to $x=0.2$ and then it decreases while H_c remains constant this may be incorporated with the calcination temperature [21]. Chae in 2001 and 2003 showed that by increasing the calcination temperature the M_s and H_c values can be increased in $\text{Co}_{1.2}\text{Ti}_{0.2}\text{Fe}_{1.6}\text{O}_4$ which confirms the direct relation of magnetic behaviour with calcination temperature [22, 23]. Patil and Kounsalye et. al. (2020) studied the effect of Ti on the electric properties of CoFe_2O_4 and showed a similar nature in that the resistivity decreases with an increase in temperature, and the dielectric parameter decreases with an increase in frequency [24]. Nlebedim, Jiles (2015) investigated $\text{Co}_{1+x}\text{Ti}_x\text{Fe}_{2-2x}\text{O}_4$ and observed that up to $x=0.3$ content at 50 K temperature the coercivity decreases but after that for $x=0.4$ & $x=0.5$ specimens, the coercivity increases. It has also been recorded that by increasing temperature from 50 K to 300 K the coercivity of the material is decreased with an increase in the concentration of Ti [25]. The effect of Ti doping in either of the interstitial sites and resultant magnetic properties can be understood by the following diagram (Figure 1).

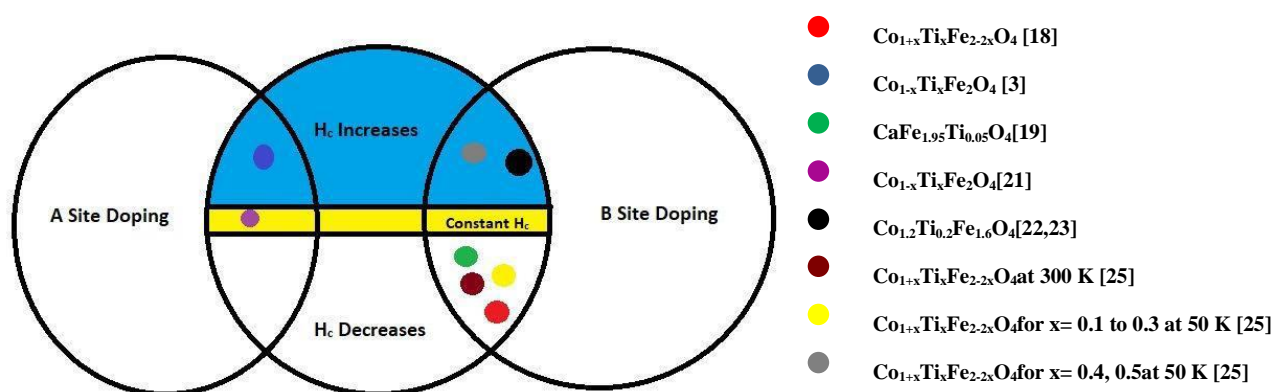


Fig 1: Diagram of Ti Doping in different sites and H_c (Coercivity) Value

Effect of Li Doping in CoFe₂O₄

Shobhna (2012) observed that as the concentration of lithium is increased in the $\text{CoFe}_{2-x}\text{Li}_x\text{O}_4$ system, the conductivity decreases [6]. While Rashid et. al. (2015) synthesized $\text{CoCu}_x\text{Li}_x\text{Fe}_{2-2x}\text{O}_4$ to record the electrical properties which are found entirely different i.e conductivity

increased with an increase in the concentration of Cu and Li in the present system [26]. Anjum et. al. (2017) doped Li in the A site and the results were quite opposite to that of doping in the B site as conductivity was increased when the concentration of Li was increased [27]. Junaid et al. (2020) prepared a $\text{LiCo}_{0.5}\text{Fe}_2\text{O}_4$ system and found that the specimen (poses soft ferrimagnetism after doping Bismuth the values of M_s & M_r were enhanced. The value of H_c was decreased when the amount of Bi was increased in B-site. The dielectric constant was also decreased when the concentration of Bi was increased [28]. Shobana, Park and Choe (2019) synthesized $\text{CoLi}_x\text{Fe}_{1-x}\text{O}_4$ and analyzed its electrical properties. It was found that by increasing the amount of Li the conductivity of the substance was also increased. It was quite opposite of $\text{CoLi}_x\text{Fe}_{2-x}\text{O}_4$ which was discussed earlier [29]. Arvind et. al. (2016) synthesized $(\text{Li}_{0.5}\text{Fe}_{0.5})_{1-x}\text{Co}_x\text{Fe}_2\text{O}_4$. From magnetic measurement, it was observed that the H_c decreases when the concentration of Li is increased. Also, from the dielectric analysis, it was observed that Li-doped systems have more dielectric constant values than that pure Co samples [30]. The variation in the electric conductivity due to Li-ion doping in the A-site or B-site can be seen in Figure 2.

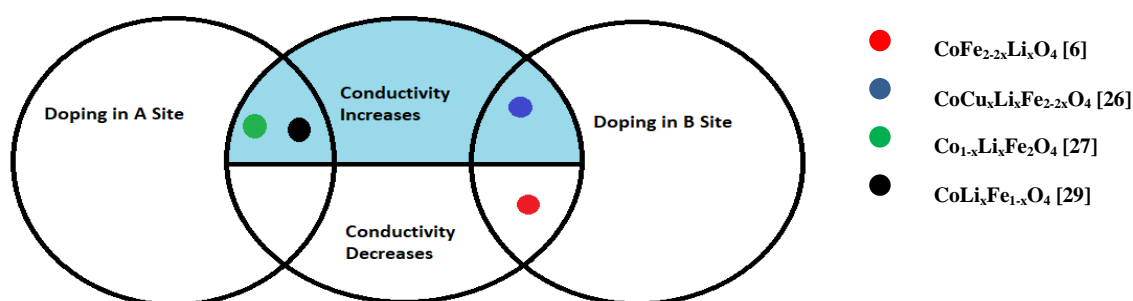


Fig 2: Diagram of Li Doping in different sites and Conductivity

Conclusion

From the collective review studies, we have concluded that by doping the Li^{1+} and Ti^{4+} in spinel ferrite materials an entirely new set of properties is found. Both magnetic and electrical properties of Li^{1+} and/or Ti^{4+} doped CoFe_2O_4 systems are dependent on doping concentration, synthesis processes and sintering temperature. As well as the properties of these types of specimens can be modulated by the interstitial sites' preferences for cations substitution.

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