ABSTRACT

Spinel compounds, AB_2O_4 (where, A and B are the divalent and trivalent cations) are attractive for their wide range of applications such as catalysts and sensors (Yamasaki *et al.*, 2006 and Tomiyasu *et al.*, 2004). While in normal spinel, the divalent cations (Mg, Mn, Ni, Zn, Co) occupy the tetrahedral (A) site and trivalent cations (Al, Cr, Fe) prefer the octahedral (B) sites, in an inverse spinel, the divalent cations prefer one of the B site and the trivalent cations are equally distributed among A and B sites. In mixed spinels, two or more different kinds of divalent cations are distributed between A and B sites. Thus, the magnetic behavior in these compounds is sensitive to the type of cations and their distribution among A and B sites of the lattice. The magnetism in spinels mainly originates from the exchange interaction of unpaired electrons between cations occupying the A and B sites. As a result, properties can be modulated and materials can be tuned for technological applications. The MCr_2O_4 (M = Mn, Co, Ni, Zn, Mg, Fe) are ferrimagnetic spinels, in which the M^{+2} cations occupy the tetrahedral sites and Cr^{3+} cations occupy the octahedral sites. One of the spinel of general formula MCr_2X_4 (M= Mn, Fe; X=O, S) exhibits many unusual magnetic properties such as ferrimagnetism, colossal magnetoresistance, magnetoelectric coupling etc. Chromites with spinel structure are focused in solid-state sciences due to their broad range of functions (Melot *et al.,* 2009). One of the chromite i.e., cobalt chromite has attracted much attention because of its multiferroic behavior as well as fascinating temperature and magnetic field dependent magnetoelectric properties (Yamasaki *et al.* 2006). The uniqueness of $CoCr_2O_4$ is as it not only displays uniform polarization and spatially modulated magnetism but also exhibits uniform magnetization in the conical cycloid state. $CoCr_2O_4$ exhibits a rich sequence of magnetic transitions such as paramagnetic to collinear ferrimagnetic ordering at Curie temperature, T_C (94 K) and non-collinear spiral ordering at T_S, 23K and finally to a lock-in transition, T_L, 15 K (*Tomiyasu et al.,* 2004).

Yamasaki et al., *Phys. Rev. Lett.* **96** (2006) 207204; Tomiyasu et al., *Phys. Rev. B* **70** (21) (2004) 214434; Tomiyasu et al., *Physica B* 392 (2007) 16-19; Melot et al., *Journal of Physics: Condensed Matter* **21** (2009) 216007; Lawes et al., *Phys. Rev. B* **74** (2006) 024413.

With decreasing temperature from 300 K, the consequence of high crystal field stabilization energy of Cr^{3+} (2.02 eV) which leads to strong anti-ferromagnetic B-B interaction over A-B (Dwight *et al.,* 1969). As a result, the anti-ferromagnetic alignment between A and B sites is completely destroyed and system exhibits a screw ordering. This is otherwise named as ferrimagnetic spiral wherein the spins lie on the conical surfaces. Some reports found on magnetic transitions focused on bulk and single crystals of $CoCr_2O_4$. Menuk *et al.* have shown in bulk sample, that below T_C, magnetic ordering consists of a ferrimagnetic component and a spiral component through neutron diffraction and magnetic measurements (Menuk et al., 1964). The ferrimagnetic component exhibits long range order at all temperatures below T_C while the spiral component exhibits a short range order. Lawes *et al.* further reports a dielectric anomaly below spiral magnetic order (Lawes *et al.,*2006). The spiral component induces electric polarization and also a spontaneous magnetization for which it is said to be as multiferroic. Tomiyasu *et al.* revisit the spiral ordering by neutron scattering and magnetic measurements in $CoCr_2O_4$ single crystals and have shown a simultaneous formation of long range ferrimagnetic component and a short range spiral component at lowest temperature phase (Tomiyasu *et al.*, 2004). Severance *et al.* have shown that with increase in temperature from 10 to 45K, intensity of the magnetic satellite peak decreases (Severance *et al.*, 1993). At 50 K, the intensity of the diffuse peak diminishes to the background level, indicating that short-range magnetic order is completely vanished. Incommensurate to commensurate transition of the propagation vector is observed at spiral ordering temperature by Plumier *et al* and Yamasaki *et al.* investigate that the compound undergoes a transition to a conical spin structure with an incommensurate propagation vector at $T_S = 26$ K, and a lock-in transition at around 15K (Plumier *et al.,* 1968). Moreover, scarce reports on $CoCr_2O_4$ generates a lot of dispute on magnetic transitions i.e. whether short range or long range, spiral ordering is whether commensurate or incommensurate etc.

Menyuk et al., *Le Journal De Physique*, **25** (1964) 528; Severance, et al., *Am. Miner.* **78** (1993) 724-732; Plumier et al., *Journal of Applied Physics* **39** (2) (1968) 635-636; Dwight et al., *Journal of Applied Physics* **40** (3) (1969) 1156-1157; Barrera et al., J. Magn. Mang. Mater. 456 (2018)372-380

It is also important to study the above facts when size is reduced to the nanometer range.It is also interesting to study the mixing A or B sites by magnetic or non-magnetic ions when size of the particles are reduced to nanometer range. In this context, Barrera *et al.*, report cation distribution effect on static and dynamic magnetic properties of $Zn_xCo_{1-x}Fe_2O_4$ powders (Barrera *et al.*, 2018). The sample with x=0.08, results with a completely inverse spinel structure where as random distribution is observed for x=0.56. The replacement of non-zero angular momentum of Co^{2+} ions with zero angular momentum Zn^{2+} ions induces a reduction of magnetocrystalline anisotropy reflected in the coercive field; whereas the mutual distribution of Co^{2+} and Zn^{2+} in the sub-lattice intensely affect the saturation magnetization following the Yafet-kittel's model. Martinho *et al.* have studied the effect of Cd doping in frustrated antiferromagnetic $ZnCr_2O_4$ single crystal. Spin glass behavior is reported in $Zn_{1-x}Cd_xCr_2O_4$(x=0.05, 0.1) samples (Martinho *et al.,* 2001) . Durgesh *et al.* have observed an enhancement in T_C up to 200 K and spiral ordering temperature up to 40 K by increasing Fe concentration up to 50% (Drugersh *et al.,*2017). Kemei *et al.* have studied magnetic transitions in normal spinel, $Mg_{1-x}Cu_xCr_2O_4$ and have reported that the Neel temperature (T_N) observed at 12.5 K at x=0 increases to 128 K at x=1(Kemei *et al.* 2012). Kemei *et al.* have reported the changes in structural ground states of $ZnCr_2O_4$ when 10% and 20% Co^{2+} cations are substituted on the nonmagnetic, Zn^{2+} site. It has been shown that when Co^{2+} ions are greater than or equal to 10%, the structural distortions that accompanies antiferromagnetic ordering in $ZnCr_2O_4$ is suppressed (Kemei *et al.,* 2014). Rich sequence of magnetic transitions such as T_C, T_S and T_L reported in few chromites, have not been studied in Zn substituted $CoCr_2O_4$ nanoparticles so far. Therefore, in the present work, we examine the role of cation distribution and their effect on structure and magnetic properties of $Zn_xCo_{1-x}Cr_2O_4$ ($0 \leq x \leq 0.8$) nanoparticles.

Martinho et al., *Phys. Rev. B* **64** (2001) 024408; Kumar et al., *Dalton Transactions* **46** (31) (2017) 10300-10314; Kemei et al., *Journal of Physics: Condensed Matter* **24** (2012) 046003; Kemei *Physical Review B* **89** (17) (2014) 174410.

The thesis is organized in to VIII chapters as follows:

Chapter I presents a brief introduction of spinels. Their structure, classification, and exchange interactions are discussed. The cation distribution in spinels is explained based on crystal field theory. A brief introduction about the chromties and their applications are presented.

Chapter II presents the literature related to $CoCr_2O_4$ and transition metal doped $CoCr_2O_4$. Various synthesis methods like, sol-gel, hydrothermal and sonochemical techniques to prepare the $CoCr_2O_4$ nanoparticles are discussed. The structural, magnetic, dielectric and multiferroic properties are presented. The literature on exchange bias, training effect and memory effect of core-shell nanoparticles have been discussed.

Chapter III describes the experimental techniques used to prepare the $Zn_xCo_{1-x}Cr_2O_4$ ($0\leq x \leq 0.8$) samples. Various experimental techniques such as XRD, SEM, TEM, XPS, EXAFS, DNS, MPMS were discussed which are used for the phase, structure, microstructure, and magnetic properties.

Chapter IV Size dependent structure, microstructure and magnetic transitions such as curie temperature (T_C), non-collinear spiral ordering temperature (T_S) and spin lock-in temperature (T_L) are studied in $CoCr_2O_4$ after reducing the size of the particles to 10 and 50 nm.

Chapter V discusses about the temperature dependent exchange bias, training effect and memory effect of 50 nm core-shell $CoCr_2O_4$ particles.

Chapter VI microstructure, cation distribution and magnetic properties of $Zn_xCo_{1-x}Cr_2O_4$ ($x=0.05, 0.1$) nanoparticles.

Chapter VII studies on microstructure, cation distribution and magnetic properties of $Zn_xCo_{1-x}Cr_2O_4$ nanoparticles in the range of $0.15 \leq x \leq 0.8$.

Chapter VIII discusses conclusions and future scope.