Preface

Spinels, AB_2O_4, a prominent class of functional materials having unique electrical, magnetic, chemical and mechanical properties show immense potential for energy storage and conversion, data storage, electronics, and catalysis. Among the spinels, Co-Mn based spinels have garnered significant research interest subjecting to their intriguing properties. In these oxides, Co and Mn both can occupy A and B site exhibiting multiple valences, effecting their properties. Generally, in $CoMn_2O_4$, tetrahedral (A) site is occupied by Co^{2+} and the octahedral (B) site is occupied by Mn^{3+}, while in case of $MnCo_2O_4$, B site is equally occupied by Co^{3+} ions and Mn^{3+}, whereas Co^{2+} is occupied the A site. Presence of Mn^{3+} in B site is accompanied with Jahn–Teller distortion in octahedral interstices and lowers the crystallographic symmetry from cubic to tetragonal. This indicates that the crystal structure of $Co_xMn_{3-x}O_4$ is sensitive to Co/Mn ratio. In $Co_xMn_{3-x}O_4$, when $0.0 \leq x < 1.1$ it shows tetragonal phase, the cubic structure is prevailed for $1.7 \leq x \leq 3$ at room temperature. The intermediate composition ($1.1 \leq x \leq 1.6$) is found to be in mixed phase of cubic and tetragonal. Having multiple valences tunable structure and electrochemical stability, these compounds are extensively studied for energy storage and conversion. However, very less attention has been paid to their structure dependent magnetic properties as $Co_xMn_{3-x}O_4$ spinels exhibit a complex magnetic behaviour showing magnetic ordering at low temperature. While Mn_3O_4 ($x = 0.00$) shows a triangular spin arrangement as suggested by Yafet and Kittel rather than obeying Neel's antiparallel spin arrangement, with substitution of Mn by Co exchange interaction between triangular spin arrangement of Mn^{3+} at B site and collinear spin arrangement of Co^{2+}/Mn^{2+} at A site induces more complexity in their magnetic behaviour. Generally, two transitions have been observed in $CoMn_2O_4$, where the low temperature transition is related to the tetragonal phase and the higher temperature transition is assigned to some impurity phase. There is a scarcity of reports explaining the second transition observed in M vs T curve. Henceforth, we have synthesized $Co_xMn_{3-x}O_4$ with varying x from 1.00 to 2.00, and investigated thoroughly the structure and local structure dependent magnetic properties. The lower temperature transition corresponds to the tetragonal phase and the higher temperature transition is assigned to the cubic phase. Further, the novel magnetic properties such as unusual high coercivity, vertical magnetization, and exchange bias are also found to be correlated with the structure. Moreover, we have examined structural properties correlation with magnetic properties after Cr doping in $CoMn_2O_4$. These studies are compiled in seven chapters which are given below:

In **Chapter 1**, we offer a concise overview of spinel, elucidating its structure, compositions, properties, and applications with a brief literature survey on spinel, $Co_xMn_{3-x}O_4$ and the effect of dopants on $Co_xMn_{3-x}O_4$ are also illustrated. Based on the literature survey, the objective of the thesis is outlined and accordingly, the results with discussions and important findings followed by conclusions are presented in subsequent chapters.

In **Chapter 2**, we present the methodology utilized for sample preparation by coprecipitation technique. The chapter also addresses characterization techniques that are used for data collection and analysis. The structure, local structure, and microstructure analysis are carried out using, X-ray diffractometer, X-ray Photoelectron Spectroscopy (XPS), RAMAN, X-ray Absorption Fine Structure (XAFS) spectroscopy, High-Resolution Transmission Electron Microscopy (HR-TEM), and Field Emission Scanning Electron Microscopy (FE-SEM). The temperature and field dependent magnetization are evaluated using MPMS-3.

Chapter 3 introduces the structure dependent magnetic properties of $CoMn_2O_4$ nanoparticles. Rietveld refinement of the X-ray diffraction pattern reveals the coexistence of 91.84% of tetragonal and 8.16% of cubic phase. While Raman spectra and SAED pattern confirm the spinel structure, both +2 and +3 oxidation states for Co and Mn are further confirmed by XPS. Interestingly, magnetic measurement shows two magnetic transitions, Tc_1 at 165 K and Tc_2 at 93 K corresponding to paramagnetic to a lower magnetically ordered ferrimagnetic state followed by a higher magnetically ordered ferrimagnetic state, respectively. While Tc_1 is attributed to the cubic phase, Tc_2 corresponds to the tetragonal phase. In contrast to general temperature dependent H_C observed in ferrimagnetic material, an unusual temperature dependent H_C with high spontaneous exchange bias of 2.971 kOe and conventional exchange bias of 3.316 kOe at 50 K are observed. In addition, a high vertical magnetization shift (VMS) of 2.5 emu/g is observed at 5 K, attributed to the Yafet-Kittel spin structure of Mn^{3+} in the octahedral site. Such unusual results are discussed on the basis of competition between the non-collinear triangular spin canting configuration of Mn^{3+} cations of octahedral sites and collinear spins of tetrahedral site.

In **Chapter 4**, we have investigated the evolution of structure and local structure in $Co_xMn_{3-x}O_4$ with varying x from 1.00 to 2.00. Rietveld refinement of the X-ray diffraction pattern indicates that the spinel nanoparticles exhibit the coexistence of tetragonal and cubic phases in the range of $1.00 \leq x \leq 1.50$, while a pure cubic phase is observed for $1.75 \leq x \leq 2.00$ at room temperature. Reduction in tetragonal phase fraction from 92 % for $x = 1$ to 47% for $x = 1.5$ is attributed to diminution of Jahn-Teller active Mn^{3+} ions occupying the octahedral site of spinel lattice. Such transition is validated with the local structure analysis where it is observed that while Mn^{3+} and Co^{2+} ions are distributed among B and A site, respectively in

$x = 1.00$, with increase in x, Mn^{3+} in B site is replaced by Co^{3+} ions. When $x \geq 1.75$, additional presence of Mn^{4+} has been observed from the EXAFS which supports the X-ray photoelectron spectroscopy (XPS) results. Magnetic properties of the samples have been investigated in next chapter.

In **Chapter 5**, we have discussed the variation in the magnetic properties of $Co_xMn_{3-x}O_4$ with varying x from 1.00 to 2.00 and correlated with the structure and local structure. In accordance with coexistence of cubic and tetragonal phases, for $x = 1.00$, two magnetic transitions Tc_1 and Tc_2 at 165 K and 93 K respectively are observed. With the increase in x, as the cubic phase grows at the expense of tetragonal phase, Tc_1 grows at the expense of Tc_2, and finally at $x = 2.0$, where pure cubic phase exists only Tc_1 is detected. Unusual temperature dependent H_C is observed for coexistence of cubic and tetragonal phase. Tetragonal phase induces high spontaneous (H_{SEB}) and conventional (H_{CEB}) exchange bias with unusually high vertical magnetization shift (VMS) than that of the pure cubic phase, shows maximum H_{CEB} of 4.062 kOe for $x = 1.5$ and a VMS of 2.5 emu/g for $x = 1$. Such dependence of VMS and exchange bias on tetragonal to cubic phase ratio in $Co_xMn_{3-x}O_4$ is demonstrated for the first time and interpreted based on the interaction between different arrangement of spins in A and B sublattice.

In **Chapter 6,** the structure and local structure dependent magnetic properties have been investigated in $CoMn_{2-x}Cr_xO_4$, where $x = 0.50$ and 1.00. Rietveld refinement indicates the transformation from dominating tetragonal phase for $x = 0.50$ to pure cubic phase for $x = 1.00$, due to substitution of Mn^{3+} with Cr^{3+}. Further, XAFS confirms that the Co^{2+} ions while occupy A site, Cr^{3+} and Mn^{3+} occupy B site in both samples. In accordance with two structural phases, for $x = 0.50$, two magnetic transitions Tc_1 and Tc_2 at 169 K and 110 K respectively are observed, for x = 1.00, only single magnetic transition T_{C1} at 128 K is detected. For x = 0.50, unusual temperature dependent H_C is observed, while x = 1.00 shows general ferrimagnetic H_C behavior. Additionally, for x = 0.50 H_{CEB} of 397 Oe and a VMS of 0.4 emu/g at 5 K is observed which is found to be absent for x = 1.00. Observed exchange bias and VMS are explained based on the Yafet-Kittel spin structure of Mn^{3+} in the B site and sublattice magnetization.

In **Chapter 7**, a comprehensive overview of the undertaken work is provided. Our focus has been on investigating the structure, local structure, and their effect on the observed novel magnetic properties in $Co_xMn_{3-x}O_4$ with varying x from 1.00 to 2.00 and Cr doped $CoMn_2O_4$. Additionally, we present future work to be done in this area.

A list of journals and books used to bind up the thesis has been given at the end as references.