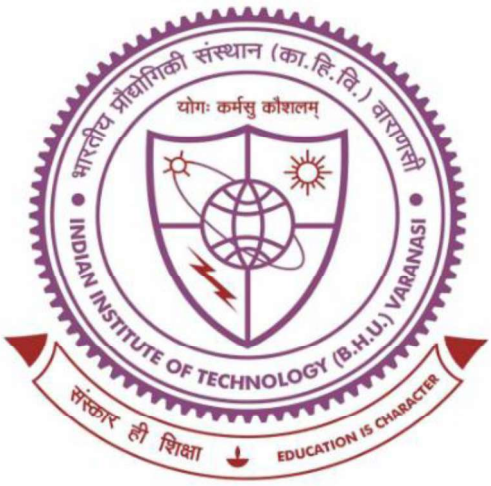
Structure and Local Structure Driven Novel Magnetic Properties of Co-Mn Based Spinel Compound



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By

Sanjna Rajput

School of Materials Science and Technology
Indian Institute of Technology
(Banaras Hindu University)
Varanasi - 221 005

Roll No: 19111503

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Chapter 7
Summary and Prospects

In the present work, we have examined the crystal structure, local structure, and magnetic properties of $Co_xMn_{3-x}O_4$ nanoparticles with varying *x* from 1.00 to 2.00 and with Cr doping in $CoMn_2O_4$. The important findings of the thesis work are outlined below.

Generally, $CoMn_2O_4$ showed tetragonal structure in bulk. In the present case, on decreasing the particle size to nanometer range, we observed coexistence of tetragonal and cubic phase. Rietveld refinement of X-ray diffraction pattern showed 91.84% of the tetragonal and 8.16% of the cubic phase at room temperature where Co and Mn occupied both A and B sites. While the XPS analysis further validated the presence of +2 and +3 oxidation states of Co and Mn, Raman active modes such as B_{1g}, A_{1g}, B_{2g}, E_g, B_{1g} and A_{1g} confirmed the spinel structure. Interestingly magnetic measurement showed that, in agreement with the two structural phases, two magnetic transitions Tc_1 and Tc_2 were observed at 165 K and 93 K, respectively, corroborated with cubic and tetragonal phases. An unusual temperature dependent H_C behavior showed a maximum at 50 K with a high H_{CEB} of 3.316 kOe and H_{SEB} of 2.971 kOe. A high VMS of 2.5 emu/g was observed at 5 K which decreased with temperature and vanished in vicinity of Tc_2. It was discussed based on Yafet-Kittel spin structure of Mn^{3+} in B site with collinear configuration of cations at A site.

The intriguing findings obtained for $CoMn_2O_4$ inspired further investigation of the Co-Mn based spinels. Consequently, a systematic evolution in structure, local structure, and microstructure was observed for $Co_xMn_{3-x}O_4$, when *x* increased from 1.00 to 2.00. X-

ray diffraction pattern indicated a coexistence of tetragonal and cubic phase for $1.00 \leq x \leq 1.50$ and a pure cubic phase for $x > 1.50$. The decrement in tetragonal phase fraction from 92 % to 47 % with increasing x from 1.00 to 1.50, was accompanied by the presence of a reduction of J-T active Mn^{3+} ions upto 55% in the B site. Microstructural measurements showed a reduction in particle size from 96 to 48 nm. In addition, XPS indicated the presence of +2 and +3 valencies for both Co and Mn for the composition having coexistence of phases, whereas, for the pure cubic phase, an additional +4 oxidation state was also present for Mn. Further, in support to this, XANES and EXAFS spectra illustrated that Mn^{3+} and Co^{2+} ions mainly occupied B and A sites, respectively, for $x = 1.00$. With the increase in x, Co^{3+} started replacing Mn^{3+} ions. When x increased to 1.75, a significant decrement in average bond length of $Mn_{B\text{-}O}$ obtained from EXAFS confirmed the presence of Mn^{4+} ions.

In agreement with the two structural phases, while two magnetic transitions at Tc_1 (165 to 170 K) and Tc_2 (93 to 101 K) were observed, single cubic phase showed a single magnetic transition Tc_1 within 176 and 167 K. In addition, an unusual decrement in H_C below 50 K was observed in the former case, and in the latter case a general H_C trend was demonstrated. The competition among the different arrangements of spins was attributed to the existing magnetic properties with particular focus on oxidation state and occupancies of Mn ions occupying the B site. Larger was the fraction of tetragonal phase, higher was the VMS. The maximum VMS of 2.5 emu/g was detected for $x = 1.00$. Although conventional and spontaneous exchange bias were evidenced irrespective of phase, a high H_{SEB} and H_{CEB} were obtained in compositions with coexistence of both tetragonal and cubic phase. It was concluded that the VMS was decided by the tetragonality induced by J-T active Mn^{3+} ions in the octahedral sublattice, however, exchange bias was controlled by the

interaction between different arrangements of spins in A and B sublattices of $Co_xMn_{3-x}O_4$ which varied with temperature and composition. Such composition driven VMS and exchange bias in $Co_xMn_{3-x}O_4$ spinel draw the attention for ultrahigh density magnetic recording devices.

$Co_xMn_{3-x}O_4$ exhibiting the intriguing structural and magnetic correlations on substitution of Mn by Co at B site, inspired to replace Mn by Cr, as Cr also has high preference for octahedral site. Consequently, Cr-doped $CoMn_2O_4$ was investigated, revealing a correlation between structural and magnetic transitions. For $CoMn_{2-x}Cr_xO_4$, Rietveld refinement indicated a transformation from a predominantly tetragonal phase (phase fraction = 89%) for $x = 0.50$ to a pure cubic phase for $x = 1.00$, attributed to the substitution of Mn^{3+} by Cr^{3+}. XAFS analysis confirmed that Co^{2+} ions occupied the A site, while Cr^{3+} and Mn^{3+} occupied the B site in both the samples. Consistent with the two structural phases, two magnetic transitions (Tc_1 at 169 K and Tc_2 at 110 K) were observed for $x = 0.50$, whereas a single magnetic transition (Tc_1 at 128 K) was detected for $x = 1.00$. Moreover, for $x = 0.50$, a conventional exchange bias H_{CEB} of 397 Oe and a vertical magnetization shift (VMS) of 0.5 emu/g at 5 K were observed. H_{CEB} and VMS were absent for $x = 1.00$, where the negative magnetization was observed. The observed VMS, H_{CEB}, and negative magnetization were associated with the Yafet-Kittel spin structure of Mn^{3+} at the B site and sublattice magnetization.

Future scope

In this thesis, a sequence of structural and magnetic phase transitions was revealed in $Co_xMn_{3-x}O_4$ ($x = 1.00$ to 2.00) nanoparticles and Cr doped $CoMn_2O_4$ particles. Besides, unusually high coercivity, vertical magnetization shift, spontaneous and conventional

exchange bias in the critical composition range of $1.00 \leq x \leq 1.50$ were demonstrated. However, several open issues need to be clarified with proper experimental and theoretical investigations. Some of the important suggestions for future works are given below.

In the current study, only room-temperature X-ray diffraction measurements under ambient pressure conditions are presented. It is crucial to precisely determine the crystal structure and magnetic transition with varying temperature and pressure through XRD, EXAFS etc.

Given the observed structure-dependent magnetic properties, detailed magnetic structural using techniques like X-ray magnetic circular dichroism (XMCD) and neutron diffraction could offer deeper insight into element-specific moment, cation distribution, and magnetic interactions in these compounds.

Such studies need to be verified in thin films of $Co_xMn_{3-x}O_4$ with varying x from 1.00 to 2.00. The investigation of the exchange bias field in thin films would be particularly relevant for potential device applications.