Chapter 7

Summary and future scope

Summary:

- We have extensively studied the effect of disorder-driven spin frustration in its magnetic behaviors in our work. In this context, we have synthesized Tb_2CoMnO_6 (TCMO) polycrystalline DP sample via conventional solid-state reaction and different characterization techniques have been performed to thoroughly investigate the system. Electronic structure analysis by XPS study reveals the presence of a mixed oxidation state (Mn^{4+}/Mn^{3+} and Co^{2+}/Co^{3+}) of B-site ions. The core level spectra of Mn 2p and Co 2p suggest the mixed valence states of Mn and Co which were also supported by the analysis of Mn 3s spectra indicating Mn ions to be in Mn^{4+}/Mn^{3+}states. The XAS study is well consistent with the XPS analysis suggesting more than one oxidation state of the B-site elements. Whereas, XAS also probes the spin state of Co i.e., Co^{2+} in HS and Co^{3+} in LS in the TCMO system. In addition, we have also performed the XMCD measurement which exhibits the magnetic nature of both the B-site element at 82 K suggesting the magnetic ordering at this temperature. The NPD) measurement is also employed to get insight into the magnetic spin arrangement for better understanding. The NPD indicates the long-range FM ordering below 100 K and the canted FM spin arrangement of the spins. The magnetic study is also well consistent with XMCD and NPD showing the FM transition at 100 K. The important aspect of this work is the dc and ac magnetization studies which reveal different interesting phases such as the GP, RSG, metamagnetic steps, and unusual slow relaxation in Hopkinson-like peak in TCMO. The inverse of dc susceptibility shows downturn behavior at low fields which suppresses as we increased the applied magnetic field. This is the prominent feature of the GP which is further confirmed by the power law. The presence of inherent ASD along with mixed valence states of B-site ions and J-T active ions are the most important ingredients for the evolution of this peculiar phase. The M(H) curve is not saturated up

to 5 T and the extrapolated saturation value is very small by the theoretical saturation magnetization. This might be the result of the presence of competing AFM/FM interactions. Moreover, M(H) curve at 25 K and 50 K also exhibits metamagnetic steps due to the drastic reorientation of the pinned domain. These domains are aligned antiparallel by the APBs at zero field. The disorder decreases the magnetic ordering, as well as the homogeneity of APBs, giving rise to sudden slope change in the hysteresis loop. This disorder further leads to spin frustration at low temperatures giving rise to the RSG. Analysis by different models yielded that the system entered a glassy state below ~ 33 K. The obtained larger value of spin-flip time (τ_0) suggests the freezing of the spin cluster instead of a single spin. Moreover, the field-dependent ac susceptibility studies unravelled the presence of the Hopkinson peak associated with the domain wall motion and the large anisotropy field. A further study yielded that the relaxation associated with this peak is unusually slow. Thus, the present system exhibits different magnetic phenomena which are mainly associated with the presence of inherent antisite disorder. We have also analyzed the temperature-dependent Raman spectra to probe into the phonon modes and the sensitive change in the local structure. These studies also provide an opportunity to look into the modification of the phonon structure, which might, in turn, shed light on spin manipulation. The Raman spectra from the 6-300 K temperature range confirm the absence of any local structural change and exhibit few Raman active modes. Whereas, the temperature-dependent Raman shift exhibit a clear deviation from the anharmonic model just below the transition temperature suggesting the SPC. The FWHM, unit cell volume, and lattice parameters indicate the absence of any magnetostriction effect. Hence, all the above facts univocally established the strong entanglement in the microscopic degree of freedom with the magnetically aligned spin i.e, SPC. We have also employed the mean-field approximation theory to ascertain the

SPC and all the preceding discussions explicitly established that there is entanglement between the lattice dynamics and the magnetic excitation through the SPC in the TCMO system. The DFT calculation well corroborated the experimental observations. Thus, the observation of such interesting properties in a single system places this system amongst the rare materials.

- In contrast to the previous work (chapters 3 and 4) in which we studied the role of antisite disorder in the ordered DP, we have prepared the $Pr_2CoFe_{0.5}Mn_{0.5}O_6$ (PCFMO) disorder DP system by the conventional solid-state route. The core level analysis of transition metals supports the mixed chemical valence state of Co, Fe, and Mn ions. Moreover, the XPS VB reveals the semiconducting nature of the system which is well consistent with the theoretical result. Further, the magnetic properties of our system reveal the existence of both AFM/FM interactions in the system. Both the interaction can be easily interpreted by the mixed-valence states which generate complexity in the system. Whereas, both dc (MT and dM/dT) and ac susceptibility studies reveal the long-range magnetic transition temperature at 187 K. The inverse dc susceptibility exhibits the presence of a GP by showing downturn behavior above the magnetic transition. The presence of coexisting phases creates the interface between FM and AFM which provokes a system to show EB phenomena. Both conventional and spontaneous EB effect is present in our system with such high values. Moreover, both the end member PCFO and PCMO only showed CEB which makes our system rich in magnetic properties. TE analysis reveals such stable EB as it decreased less than 1% in the third consecutive loop. Structural analysis of the Pnma space group at room temperature Raman spectra is well consistent with the XRD result. Further, the peak positions of phonon modes deviate from the anharmonic behavior near magnetic transition as it shows sudden softening of the phonon modes. This deviation is well supported by

FWHM analysis which excludes the possibility of magnetostriction effect induced phonon anomaly. Whereas, renormalized phonon frequency and normalized magnetic moment model given by mean-field approximation are also incorporated in the present study. Both renormalized phonon frequency difference and normalized magnetic moment follow the same trend according to mean-field approximation which confirms that there is an interplay between phonon modes and magnetic spin. Thus, the present system PCFMO display spectrum of magnetic properties which is essential for the applications.

- Next, we thoroughly investigated the A quasi 1D noncentrosymmetric spin-chain compound BMVO by employing dc magnetization, NPD, XAS, and temperature-dependent Raman spectroscopy measurements, which were accompanied by comprehensive *ab initio* DFT calculations. Unlike most of the low-dimensional spin-chain compounds, BMVO exhibited a long-range AFM ordering at a sufficiently higher transition temperature, i.e., T_N=38 K, which was confirmed by the dc magnetization and NPD measurements. The NPD data analysis yielded a collinear AFM spin structure with the nearest-neighbor spins having an AFM-coupling along the screw-chain axis of the system, whereas the spin direction lies along the *a* or *b*-axis. The analysis further suggested that the AFM order in this spin-chain system develops with an unconventional critical exponent β=0.21. Moreover, a short-range magnetic ordering much above the T_N has been observed both from the dc magnetization and NPD studies, which is triggered by the intrachain interactions upon lowering the thermal energy. The temperature-dependent Raman spectroscopy measurements unravelled the exhibition of an SPC effect below T_N for at least two phonon modes. On the other hand, an unusual thermal evolution (such as violation of the anharmonic law and apparition of peak-splitting) of the Raman modes above T_N is observed, which seemingly emanates from

the short-range magnetic ordering. Furthermore, the *ab initio* DFT calculations predicted an insulating AFM ground state of the system, which is in line with the experimental results. Theoretical calculations have also been done to estimate various possible exchange interactions in BMVO, which showed the nearest-neighbor intrachain exchange interactions are the most dominating interactions to stabilize the observed AFM ground state in BMVO.

Future Scope:

- For the B-site disordered DP systems, detailed magneto-transport and magneto-dielectric studies can be carried out to investigate if it also shows such effects. We are also exploring the dielectric behaviour of our system. As a matter of fact, it is well-known that the epitaxial growth of the thin films by pulsed laser deposition technique produces highly B-site ordered DPs. It does not require the large differences between the charge states and ion radii of the B-site ions of such DP materials. Hence, furthermore, epitaxial growth of the thin films of these B-site disordered DPs can be done to study the effect of largely reduced B-site disorder on its magnetic properties. It will also allow us to fabricate magnetic devices based on their multi-functional properties so that they can finally apply to real life. Further, we are also searching for the materials for the room temperature magnetic ordering and the other magnetic phenomena such as magnetoresistance and giant stable EB so that they can be used in practical applications.