8.1 Conclusion of the thesis

- The polycrystalline sample of geometrically frustrated pyrochlore $Eu_2Ti_2O_7$ has been grown by solid state reaction route. The dc magnetization study showed the presence of strong single ion anisotropy in the system which effectively comes into play below 90 K. The ac susceptibility study unravelled a new prominent spin freezing transition occurring near ~35 K which is the highest temperature at which such spin freezing transition could be observed in similar systems (T_f~16 K for $Dy_2Ti_2O_7$ was the maximum). The analysis by different models ruled out the possibility of spin glass transition in the observed glassy peaks and equivocally established "the single ion freezing" mechanism to be responsible for the observed transition. The non-magnetic dilution study further confirmed the single ion spin freezing process.
- Further to investigate how the 3*d*-4*f*interactions affect the spin dynamics of $Eu_2Ti_2O_7$, Fe is substituted in Eu site. The electronic structure study by X-ray absorption study (XAS) of this system $Eu_{2-x}Fe_xTi_2O_7$ (x=0.0, 0.1 and 0.2) revealed that a large octahedral distortion is present in the TiO_6 octahedra in pure $Eu_2Ti_2O_7$. The distortion is caused by the presence of an interstitial anionic site 8a near Ti^{4+} site. The Fe substitution is observed to reduce the octahedral distortion appreciably by promoting anionic migration from 48f/8b site to the vacant site 8a, thus leading to the anionic disorder in the system. This in turn results in modification in the crystal field and thus affecting the spin freezing transition. The Fe substitution is observed to largely suppress the single ion freezing transition which is also related to the faster spin relaxation of the Fe spins. It also raises ferromagnetic interactions in the system by enhancing the dipolar interactions. A solely field induced sharp transition (exclusively related to the Fe^{3+} ion substitution) is also observed at lower temperature which is

seemingly associated to the formation of some oppositely spin polarized regions raised by the dipolar interactions. Hence, the spin relaxation associated to the observed transition is found to be unusually slow.These results indicate the need for detailed study of such systems with combination of different magnetic ions on the single frustrated lattice which has potential to give rise to low temperature exotic states which is absent in similar systems with single magnetic element.

- In contrast to the above two chapters (3 and 4) dealing with the geometrical spin frustration driven magnetism, in the next chapters (5 to 7) we have extensively studied the effect of disorder driven spin frustration in its magnetic behaviours. The electronic structure study of a B-site disordered double perovskite (DP) system Pr_2CoFeO_6 by X-ray photoemission spectroscopy (XPS) and X-ray absorption spectroscopy (XAS) revealed trivalent oxidation states for the Co and Fe ions. The analysis further suggested a non-magnetic low spin state of the Co^{3+} ions. The valence band spectra analysis yielded an insulating nature of the system by showing mere absence of electronic states across Fermi level. The magnetization study showed that a magnetic transition from the paramagnetic to antiferromagnetic state occurred near ~269 K which is related to the long range AFM ordering of Fe spins. The Raman spectroscopy study showed that the system is B-site disordered as was predicted by its electronic structure. The temperature dependent Raman spectroscopy study unravelled the existence of strong spin-phonon coupling occurring for at least two phonon modes (stretching and anti-stretching) due to the re-normalization of the lattice vibration by magnetic ordering. The temperature dependent neutron diffraction study ruled out the role of the magnetostriction effect on the observed anomalous behaviour of the phonon modes near the magnetic ordering temperature. The observation of the strong

spin-phonon coupling at multiple phonon modes is very scarce and thus is very interesting.

- Next, we have thoroughly investigated the magnetic properties of Pr_2CoFeO_6 (PCFO) by neutron diffraction, dc and ac magnetization measurements as well as its theoretical density of states studies by ab initio calculations. The DOS study predicted an insulating antiferromagnetic ground state of PCFO. It also suggested for a LS non-magnetic state of Co^{3+} ions. The neutron diffraction study revealed a canted G-type of antiferromagnetic ordering below the magnetic transition temperature. The moment analysis yielded non-magnetic LS states of Co^{3+} ions, thus corroborating earlier results. The dc magnetization study revealed the emergence of a Griffiths like phase above the magnetic ordering temperature (~269 K) extending up to 370 K above which it enters in a purely paramagnetic state. The observation of the Griffiths phase in antiferromagnetic system is unconventional and rare, thus is very interesting. The spin dynamics study by ac susceptibility measurements revealed that the system enters in a re-entrant cluster glass state below 34 K owing to the existence of the B-site disorder and spin canting in the system. The system also exhibited the exchange bias effect owing to the co-existence of the antiferromagnetic state and the lower temperature glassy states. Thus, the observation of so many interesting properties in a single system places this system amongst the rare materials.
- We have also investigated the physical properties of a partially disordered heterovalent hole doped system $Pr_{2-x}Sr_xCoMnO_6$ (x=0.0, 0.3 and 0.5). The electronic structure study by XPS and XAS measurements showed that Co and Mn ions exist in mixed valence states in both the pure and hole doped systems. The hole doping increased the overall oxidation states of the B-site ions. The valence band spectra analysis indicated an insulating nature of the systems. The transport study revealed

insulating nature of the samples. It also showed that the career concentration got enhanced by Sr substitution, thus supporting the XPS/XAS results. The dc magnetization study showed the existence of the Griffiths like phase emanating mainly from the B-site disorder and quenched disorder created by the Jahn-Teller active ions. The spin dynamics study by the ac susceptibility measurements further showed the existence of two ferromagnetic transitions owing to the ordered phase (Co^{2+}-O^{2-}—Mn^{4+}) and the disordered phase (Co^{3+}-O^{2-}—Mn^{4+}). On increasing the hole doping, the ferromagnetic transition related to the ordered phase got systematically suppressed. The spin dynamics study by ac susceptibility study showed that all the pure and doped systems enter in a glassy state below 40 K which is related to its inherent anti-site disorder. However, on increasing hole doping, a cluster glass state is observed to progressively evolve immediately below the long range ordering transition. Therefore, the dual magnetic glassy states are observed in the hole doped system which is very rare and thus is important. However, unlike the lower temperature (< 40 K) conventional spin glass transition, the Sr doping induced glassy transition is realized to be a cluster glass state. The isothermal magnetization study at 5 K showed that the 25% Sr doped system (x=0.5) exhibits giant exchange bias effect owing to the presence of multiple magnetic phases.

8.2 Future perspective

In future, detailed theoretical study to explore the exact origin of the observed spin freezing transition in structurally ordered pyrochlore $Eu_2Ti_2O_7$ can be done. Other experiments like M**ö**ssbauer spectroscopy and neutron diffraction study can also be performed to elucidate the exact origin of the observed geometrical spin frustration driven spin freezing transition. Again, substitution of non-magnetic Sn^{4+} in Ti site can

be done to investigate how this affects the spin freezing of the Eu^{3+} spins by altering crystalline field.

For the B-site disordered double perovskite systems, detailed magneto-transport and magneto-dielectric studies can be carried out to investigate if it also shows such effects. Neutron diffraction study and theoretical DFT calculations can be performed on the $Pr_{2-x}Sr_xCoMnO_6$ system to investigate the exact origin of the double glassy states in this 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 double perovskites. It does not require the large differences between the charge states and ion radii of the B-site ions of such double perovskites materials. Hence, furthermore, epitaxial growth of the thin films of these B-site disordered double perovskites 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 it can finally be applicable to the real life.