Preface

Rare earth (RE) based permanent magnets are an integral part of electromechanical conversion systems like turbine generators, loudspeakers, hard disk drives, actuators, etc., thereby making them an inseparable part of modern day human's life. However, a rare earth metal crisis in 2011 compelled the researchers to search for alternatives to these RE based permanent magnets. Despite the desirable magnetic properties of rare earth (RE) magnets, they have inherent issues such as price volatility and source concentration. Further, the requirement for "gap magnets", with $(BH)_{max}$ i.e. energy products in the range of (5-30 MGOe) have prompted the search for alternative hard magnetic materials. In this regard, Mn-Bi system has received considerable attention from researchers. The low-temperature crystallographic phase (LTP) of MnBi (hexagonal $B8_1$, P63/mmc, crystal structure) possesses desirable high magnetocrystalline anisotropy (~1.6 MJm^{-3}) at room temperature. It also has a unique positive temperature coefficient of coercivity, i.e., intrinsic coercivity linearly increases with temperature up to 530 K, thus making it ideal for application at elevated temperatures. The theoretically calculated (BH_{max}) of LTP-MnBi is around 18 MGOe, with a theoretical saturation magnetization of around 81 emu/g.

Although LTP-MnBi holds promise as a potential "gap magnet," its single-phase synthesis has proven difficult as it results from an incomplete peritectic reaction at 446 ºC, resulting in the presence of undesired non-ferromagnetic secondary phases (such as elemental Mn and Bi) alongside the desired LTP-MnBi (a line compound). Various techniques including rapid solidification, chemical synthesis, sintering, and mechanical alloying, have been investigated to attain high-purity LTP-MnBi. Mechanical alloying, in particular, is commonly employed as it reduces the particle size of MnBi through milling, thereby enhances the coercivity with a compromise of its M_S values.

Considering that the achieved BH_{max} value for the bulk MnBi system is currently less than half of its theoretical value, ongoing efforts are focused on improving this performance. Various strategies such as elemental substitutions, exchange coupled magnets etc. have been investigated to enhance the magnetic properties of the MnBi system. As suggested by Kneller and Hewig, exchange-spring magnets comprised of a magnetically hard phase and a soft phase, where exchange interaction results in enhanced energy product. In fact, the micro-magnetic simulation studies predicted the possibility of an energy product, as high as 40 MGOe, in case of perfect ferromagnetic exchange interaction between MnBi and α-Fe nanocomposite system. The researchers have explored α-Fe and FeCo as soft phases with MnBi thin films with partial success. However, there have been limited investigations of unconventional, better oxidation resistant soft materials, such as Fe_3C@C, FeNi@C, and Co@C. In this study, the potential of these candidates for the soft phase in nanocomposites is evaluated. Additionally, the objective is to investigate the synergistic effects of these soft phases on the magnetic behaviors of LTP MnBi.

This thesis comprises of seven chapters:

Chapter 1 introduces the current state-of art literature and the need pertaining to "rare-earth free permanent magnets", with focus on Mn-based systems. Apart from giving an overview on the saga of commercial permanent magnets, it also deals with the properties expected from the proposed "Gap Magnet", free from rare-earth elements. It illustrates the reasons for Mn-Bi system catching the attention of researchers. Further, it provides a literature review on the efforts being carried out for the preparation of the most promising

MnBi based bulk magnets. The inherent challenges and the solutions proposed are also highlighted. Amongst the proposed solutions, discussion on exchange-spring magnets is made, which involves a composite consisting of a soft magnetic phase contributing high saturation magnetization and a hard magnetic phase with high coercivity values. The various available soft magnetic phases according to literature, conditions for the proper exchange coupling between hard and soft phases are also discussed. The objectives of the thesis work are also listed in this chapter.

Chapter 2 deals with the various synthesis methods utilized for the preparation of MnBi alloys, Fe_3C@C, FeNi@C, and Co@C nanoparticles and their nanocomposites. Further, to analyse the synthesized materials, this chapter also explains the experimental designs and material characterization tools employed. The formulae and software used for the data interpretation, along with pictorial description are also discussed.

Chapter 3 explains the effect of room-temperature high-energy ball milling on the magnetic properties of LTP MnBi phase. It also explores the effect of varying Mn percentage on the formation and magnetic properties of the phase of interest i.e. LTP MnBi. The chosen $Mn_{55+x}Bi_{45-x}$ (x = 0, 1, 3, 5, 8) alloys, after milling, exhibit a fascinating hitherto unreported, “spontaneous exchange bias”, (SEB) phenomenon. Though all the milled samples exhibited SEB, a maximum spontaneous exchange bias of 1200 Oe was obtained. As SEB enhances the coercivity and consequently their $(BH)_{max}$ in permanent magnets, the probable underlying physical mechanism of associated SEB effect is also described in this chapter. Further, high coercivity values of 7.5 kOe was achieved after 8 h of milling in one of the milled alloys. However, the M_S and M_r values decreased with milling. It was understood from the chapter that the surface oxidation, LTP decomposition during milling and low M_S

values owing to antiferromagnetic interactions of Mn are the major challenges associated with room-temperature milling of MnBi alloys.

Chapter 4 describes the attempts made to address the hurdles identified in the ambient temperature milling of MnBi alloys. This chapter deals with the study of the influence of cryogenic ball milling on the magnetic properties of LTP. It also attempts the possibility of developing exchange spring magnets with LTP as the hard magnetic phase and Fe_3C@C nanoparticles as the soft phase. It explains the two step synthesis method of Fe_3C@C nanoparticles with remarkable M_S value of ~150 emu/g. The carbon coating of ~5 nm around Fe_3C particles was observed using TEM, which provides corrosion resistance and thereby avoids deterioration of its magnetic properties. For a comparative study, MnBi/Fe_3C@C nanocomposites were prepared using both cryo-milling and room temperature milling techniques. The SQUID based magnetic analysis revealed that the cryo-milled samples exhibited superior properties, particularly the nanocomposite with a 10 wt.% addition of Fe_3C@C, demonstrated a H_C value of 6.6 kOe, M_S value of 57 emu/g, and M_r value of 35 emu/g. Spin tunneling might have aided in the exchange coupling between MnBi and Fe_3C in the presence of a carbon nanolayer. The composite's strong initial magnetization was mostly attributed to Fe_3C@C, while the carbon component enhanced its resistance to oxidation, since no oxide phases were found in the composites.

Chapter-5 deals with the improvement of energy product of the overall MnBi system by preparing its exchange coupled magnets with FeNi@C nanoparticles (varying compositions = 5, 10, 15 and 20 wt. %) via cryogenic ball milling route. Out of these, the nanocomposite with MnBi and 15 wt.% FeNi@C provided a coercivity value of 7.9 kOe with M_S and M_r values of 63 emu/g and 38 emu/g respectively upon 2 h of cryo-milling.

After the addition of the latter component, the saturation magnetization, coercivity and remanance improved by 53, 18 and 90% respectively as compared to MnBi produced by similar method. This was feasible due to the exchange coupling amongst the two phases through carbon layer. The fcc FeNi@C phase (M_S = 147 emu/g) was produced by wet chemical method followed by calcination in N_2 atmosphere at 700 °C with ethylenediamine. The results obtained in the present study surpass previous room temperature milling studies for isotropic particles and the composites of MnBi/Fe_3C@C. These considerable enhancements in values suggest that sufficient coating of carbon onto the FeNi grains facilitated the exchange coupling between MnBi and FeNi. Thus, FeNi@C emerged as an attractive option, apart from the conventionally utilised Fe/FeCo phases as a soft magnetic phase, for the production of exchange-spring magnets.

Chapter-6 contains the preparation of MnBi/Co@C exchange-coupled nanocomposites. Since the nanocomposites prepared in earlier chapters suffered from reduction of coercivity upon increasing the soft phase content, the Co@C nanoparticles were envisaged as a soft phase owing to its high anisotropy field. The Co@C nanoparticles with a mixture of hcp and fcc structure was synthesized using sol-gel technique followed by calcination. The soft phase displayed M_S value of 140 emu/g, M_r ~ 3.4 emu/g and H_C~ 14 Oe. The $Mn_{55}Bi_{45}$/Co@C composite displayed the best properties with a H_C of 10.8 kOe, M_S ~ 67.5 emu/g and M_r ~40.3 emu/g were achieved for $Mn_{55}Bi_{45}$ with15 wt.% of Co@C. This suggests that the Co@C has better exchange coupling with the LTP MnBi phase.

Chapter-7 provides the overall summary deduced from the work done and major conclusions drawn from the present investigation. It also has some recommendations for the future work, which may be explored further for better understanding as well as commercialization of LTP MnBi based materials.