CHAPTER I
INTRODUCTION

1.1 Background and motivation

Permanent magnets can maintain magnetic flux in the absence of an external magnetic field. This suggests that a permanent magnet has the potential to generate energy. They play an important role in modern technology related to energy conversion (Mohapatra and Liu, 2018). Permanent magnets are commonly used in everyday life, such as refrigerator magnets. dynamos, motors, sensors, and transducers as well as storage devices. In modern world, environment becomes important issue. There are increasing demands for high-performance permanent magnets in environmentally friendly technologies such as high-performance permanent magnet motors for hybrid and electric vehicles, performance dynamo for wind turbine, and future magnetic refrigerators and magnetic air conditioners

Nd-Fe-B and Sm-Co magnetic materials have long popularity over time in the permanent magnet industry due to their properties superior to other magnetic materials such as high energy product ($(BH)_{max}$) and low cost. However, these materials containing rare earths and thus have obvious disadvantages, such as poor corrosion resistance, loss of magnetic properties when the temperature rises (Li et al., 2018). In addition, according to a 2011 US Department of Energy report (Energy, 2010), rare earth elements, particularly Nd and Sm, are in critical supply. Mining of these elements lead to environmental problems. To alleviate such problems, rare earth free permanent magnets are therefore an option. Although the theoretically predicted $(BH)_{max}$ values for rare earth free magnetic materials are less than that of rare earth magnetic materials, the aforementioned disadvantages of rare earth magnets provide additional incentives and attract more attention to research and develop rare earth permanent magnets (Patel, Zhang and Ren, 2018).

Low-temperature phase Manganese Bismuth (LTP-MnBi) is a rare-earth-free ferromagnetic material with high coercivity and large positive temperature coefficient (Li et al., 2018; Liu, Wang and Dong, 2018), which are the desired properties for magnetic materials to be used for producing permanent magnets operating at relatively high temperature (Yang et al., 2002). LTP-MnBi is also a promising material to be as a hard phase in permanent magnet nanocomposites (Yang et al., 2002). In the recent decades, great efforts of many research groups have been devoted to the synthesis of the single phase LTP-MnBi compound. It has been theoretically predicted that its $(BH)_{max}$ could be as high as 17.7 MGOe at 300 K (Park et al., 2014). There has been reports that the single phase LTP-MnBi nanoparticles could be produced via chemical techniques with a high remanence ratio (M_r/M_s) and high coercivity (H_c) (Kirkeminde, Shen, Gong, Cui and Ren, 2015; Liu et al., 2018; Rama Rao, Gabay, Hu and Hadjipanayis, 2014; J. Sun et al., 2016). Arc-melting or melt-spinning process with subsequent grinding and thermal annealing has been employed to synthesize relatively high-purity LTP-MnBi over 90 wt%. The experimental value of the $(BH)_{max}$ of the magnetically aligned samples was reported to be 50–86% of the theoretical value with an H_c of 7.11–18.2 kOe at room temperature.

It has been demonstrated that MnBi powders with H_c values up to 3.4 kOe could be prepared by sintering at 700 °C under helium ambient (Adams, Hubbard and Syeles, 1952). There has also been a report that the magnetically aligned MnBi samples sintered at 1000 °C in an argon atmosphere exhibited a considerable H_c of 14 kOe (Yang et al., 2002). Despite being a simple method, high-temperature sintering still requires high energy and post-sintering treatments because of the formation of high-temperature phase MnBi (HTP-MnBi) at temperatures above 350 °C (Jun Cui et al., 2018). Therefore, low-temperature sintering method was applied to avoid such difficulties. Magnetically aligned MnBi with a reported H_c of about 16 kOe has been produced by sintering at 1000 °C for 10 days under high pressure in an evacuated glass capsule (Kishimoto and Wakai, 1977). A spark plasma sintering followed by long-term annealing in argon gas (up to 28 days) was also used to produce MnBi powder with H_c of 5.7 kOe (Ko, Choi, Yoon and Kwon, 2007).

Synthesis of single phase LTP-MnBi by sintering is very challenging due to its complex phase diagram resulting in segregation of Mn from MnBi during a peritectic reaction as well as the formation of HTP-MnBi upon cooling down (T. Chen, 1974). Hence, the unreacted Mn and Bi phases are commonly detected along with the LTP-MnBi phase (J. Cao et al., 2019). Owing to the low melting point of Bi (~271 °C) compared to Mn (~1246 °C) (Antonov and Antropov, 2020), the formation of LTP-MnBi at temperature above the Bi melting point involves the rearrangement of Mn powder particles in liquid Bi, liquid–solid interactions at the liquid–solid interface and diffusion of Bi into the bulk. Details of solid–liquid diffusion and isothermal solidification in several metals in a transient liquid phase during sintering were studied (Corbin and McIsaac, 2003). It is natural to explore possible ways in which large-scale MnBi might be synthesized by exploiting the solid–liquid diffusion mechanism. The minimum sintering temperature is determined by the eutectic temperature (262 °C, at which Bi-rich liquid ⟶ Bi + MnBi) where the peritectic temperature (359 °C, Mn1.08Bi + Bi-rich liquid ⟶ MnBi) is the upper limit (Si et al., 2019). So, the temperature range between 262 and 359 °C is considered to be optimal between the highest diffusion rate and the lowest HTP-MnBi formation. Analytical treatment of the sintering process in this temperature range is difficult because of the coexistence of vapor, liquid and solid phases: they must treat at once solubility, viscosity and diffusivity (Gupta, Anil Kumar and Khanra, 2018). But by assuming that the diffusion process is the rate-limiting mechanism of MnBi formation, recent research has reported that the diffusion coefficient of 1×10^{-12} cm^2/s at an annealing temperature of 300 °C, which was deduced from the SEM observations of the decrease in size of Mn inclusions in the bulk LTP-MnBi prepared by arc-melting process (Van Nguyen and Nguyen, 2017). This value is rather high and, thus, not applicable for explaining the diffusion during MnBi formation by sintering, which obviously occurs at much smaller formation rate.

It is essential that the magnetic stability is one of the most important factors shall fully be investigated prior to launching a new type of permanent magnet. Generally, the magnetic properties were degraded mainly due to the oxidation (Janotová, Švec, Maťko, Janičkovič and Sr., 2018; Ly et al., 2014; Villanueva et al., 2019) and decomposition (Ly et al., 2014; Sun, Xu, Liang, Sun and Zheng, 2016) upon experiencing to humidity (Jacobson and Kim, 1987) and elevated temperatures (S. Cao et al., 2011; Y.-C. Chen et al., 2015; J. Cui et al., 2014; Zhang et al., 2014) for an extended period of time. It was found that the magnetic performance of LTP-MnBi could be degraded even in ambient atmosphere with different rates depending on its physical forms or shapes. Sun et al. reported the magnetic degradation in ambient atmosphere at room temperature of the LTP-MnBi thin film prepared by magnetron sputtering system. They found a 35% saturation magnetization (M_s) reduction with slight coercivity (H_c) enhancement after exposure to air for 14 days. These behavoiurs were explained by the oxidation of Mn and the weakened inter-grain exchanges at grain boundaries (M. Y. Sun et al., 2016). Villanueva et al. also reported that the ferromagnetic property of LTP- MnBi thin film prepared by DC-magnetron sputtering were reduced for up to 54% and 100% after exposing to the air for 6 days and 4 months explained by the MnBi phase disappearance (Villanueva et al., 2019). The dramatic degradation in the melt-spun LTP-MnBi ingot were reported after exposing to the air for 7 days which were explained by the Mn oxidation leading to the MnBi decomposition (Ly et al., 2014). The magnetic phase content of MnBi ribblon flakes decreases after exposure to ambient atmosphere for 1 year respected to oxidation. A chemical composition of surface sample was investigated by EDS map. They found Bi-rich phases segregate after 6 months and the top of master alloy surface is covered by oxygen layer (Janotová et al., 2018).

Several techniques, such as surface modifications and surface capping, have been utilized in order to stabilize the magnetic performance of LTP-MnBi. The aim of such modifications is to prevent the MnBi from oxidation and decomposition. For example, Sun et al. found that their Ta capped MnBi were significantly more stable than the bare MnBi. The H_c and M_s were kept unchanged after 14-day exposure to air (M. Y. Sun et al., 2016). The cross-sectional MnBi bulk prepared by zone-melting in a He atmosphere was studied. It does not slightly exhibit oxidation after exposure to air more than 1 year due to nearly Mn free-MnBi ingot (Yoshida, Shima, Takahashi and Fujimori, 1999).

This thesis work focused on the investigation of LTP-MnBi sintered in vacuum at low temperature. The crystal structure, morphology, and the magnetic properties of the sintered LTP-MnBi were studied. More importantly, this is the first time to carry out in-depth investigation of the formation mechanism for LTP-MnBi prepared by low-temperature sintering in vacuum and thermal stability of the sinter MnBi. It was expected that the diffusion process is the main factor for controlling the LTP-MnBi layers formed during sintering. In this work, a new approach was adopted to determine the diffusion coefficient in sintered LTP-MnBi powder particles from the results taken by energy dispersive spectroscopy (EDS) line scan measurements of cross-sectional MnBi powder particles. The long-term magnetic stability at room temperature and decomposition at elevated temperature of the vacuum sintered LTP-MnBi samples were also investigated for the first time. The details of magnetic properties, crystal structure and chemical composition were obtained by various material characterization techniques.