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ABSTRACT
Nonmagnetic phase assisted low temperature phase MnBi bulk magnetic materials, i.e., MnBi/NaCl and MnBi/C magnets, were fabricated by hot pressing mixtures of MnBi and NaCl or C powders. The effects of nonmagnetic NaCl or C on the magnetic and physical properties of the MnBi bulks were investigated in detail. Identifications of phase stability and decomposition rate during the mixing and hot pressing processes were analyzed using the Rietveld refinement method. It was found that the coercivities ($H_c$) of the bulk magnets significantly increase with increasing content of NaCl or C: $H_c$ of the MnBi bulks with NaCl of 5 wt. % and C of 5 wt. % reach 9041 Oe and 7054 Oe, respectively, which are higher than the pure MnBi bulk of 6272 Oe. This means that the addition of a small amount of NaCl and C in the MnBi bulks could be one of the promising routes to enhance their magnetic properties.

I. INTRODUCTION
Rare-earth free permanent magnets are attracting increasing research interests with increasing costs of rare-earth resources. As a rare-earth free permanent magnet, ferromagnetic low temperature phase (LTP) MnBi (space group $P6_3/mmc$) has emerged as the most promising candidate for high temperature applications among all the rare-earth free permanent magnetic materials due to its high uniaxial magnetocrystalline anisotropy constant ($K$) and unusual positive temperature coefficient of coercivity ($H_c$). To achieve high $H_c$ in LTP MnBi, it is necessary to reduce the particle size down to its single domain size of 1 μm. In general, the mechanical milling process is effective to reduce the particle size, but high energy ball milling causes a phase decomposition and distortion, which results in the reduced magnetization ($M$). High purity LTP MnBi up to 98 vol. % was achieved by the melt spinning process. Although the melt spinning process with additional ball milling and grinding processes lead to high $H_c$ in MnBi powders, the $H_c$ reduction when consolidating the powder to a bulk magnet is a serious problem that must be overcome. Recently, a method of using second magnetic materials such as Fe-Co and Sm-Fe-N to occupy grain boundaries of the MnBi bulk magnet to produce magnetically exchange coupled high performance hybrid magnets was attempted. However, to the best of our knowledge, there is no report on a nonmagnetic phase assisted MnBi bulk magnet, except the Bi phase decomposed from MnBi alloys.

Therefore, in this work, we have performed the low energy ball milling (LEBM) process to decrease the particle size of the LTP MnBi powders with minimized $M$ reduction and added nonmagnetic phases into the MnBi bulk magnet to increase $H_c$. As the nonmagnetic phases, NaCl and C were selected due to their easy availability and grindability.

II. EXPERIMENT
The LTP MnBi was synthesized using the solid-state reaction method. High purity manganese (Mn 99.95%) and bismuth (Bi 99.50%) powders with size ranging from 25 to 75 μm were mixed...
using the Turbula shaker mixer for 1 h. In order to increase the contact area between the particles, the mixed powders were loaded into a mold of 10 mm in diameter and pressed under 110 MPa. To promote the solid state diffusion and obtain a high purity LTP MnBi alloy, the as-pressed pellets were consecutively annealed at 265°C for 3 h and at 350°C for 72 h in an argon atmosphere. The as-annealed pellets were crushed and manually ground to obtain LTP MnBi coarse powders. The powders were then LEBM for 2–8 h to obtain microsized powders and optimize magnetic properties.

The optimized ball milling condition was applied to uniformly mix the MnBi powders and high energy ball milled NaCl or C powder in two different ratios of 98 to 2 wt. % and 95 to 5 wt. %. The mixtures were loaded into a stainless steel jar in a glove box to prevent them from oxidation. The ball to powder weight ratio was set to be 10–1, and approximately 50 vol.% of the jar was filled with ethyl alcohol as a surfactant. After the ball milling, the powders were dried in vacuum and collected in the glove box. The dried mixtures of the MnBi and NaCl or C were then loaded into a mold and pressed under 450 MPa at 320°C under vacuum condition.

The crystalline structure and phase purities of the products were characterized by using X-ray diffraction (XRD) with Cu-Kα (λ = 1.5406 Å) radiation, and the measured XRD patterns were analyzed by using the Rietveld refinement method with the FULLPROF program. The morphologies of the powders were examined with a field emission scanning electron microscope (FE-SEM), and the surfaces of the bulk were examined with a scanning electron microscope (SEM). The elemental distributions of the bulk samples were examined using energy dispersive spectroscopy (EDS). Densities of the bulk samples were calculated using Archimedes’ principle. The powder samples were aligned with the paraffin in an applied magnetic field of 4 T by using a Quantum Design physical property measurement system (PPMS) before measuring magnetic hysteresis loops, while the bulk samples were measured as loaded on a sample holder. The magnetic properties of the bulk samples were corrected with the demagnetization factor 0.1983 according to the shape of the bulk samples.

### III. RESULTS AND DISCUSSION

In order to effectively reduce the particle size without phase decomposition of LTP MnBi, the LEBM process was employed to prepare fine MnBi powder to fabricate bulk magnets. To maintain a high LTP MnBi content and optimize the ball milling condition for maximized $H_c$, the MnBi powders were LEBM for 2, 4, 6, and 8 h. We have found that the LEBM powders for 4 h has the highest coercivity ($H_c$) compared to the other powders.

The microsized LTP MnBi powder was then hot pressed to produce high density MnBi bulk magnets. In order to decrease the phase decomposition and oxidation, while increasing the density, the MnBi powders were hot pressed under 450 MPa at 320°C in vacuum condition. It is noted that the pressing temperature is higher than the solidus temperature of the eutectic reaction between Bi and MnBi, i.e., 262°C, but lower than the phase transformation temperature of 355°C to high temperature phase (HTP). Mn tends to segregate from MnBi liquid through the peritectic reaction at 446°C.

Figure 1 shows the refined XRD patterns of the LEBM powder for 4 h and hot pressed MnBi bulk, which were analyzed using the Rietveld refinement method to investigate the phase identity and weight fraction. From the refined XRD patterns, the LEBM powders were found to have hexagonal structure with the space group $P6_3/mmc$ and the lattice constants $a_0$ and $c_0$ were 4.285 ± 0.001 and 6.115 ± 0.001 Å.
respectively. The LEBM powders and hot pressed MnBi bulk were mainly composed of LTP MnBi, while the peaks around 27.21° and 42.97° were analyzed to be impurity Bi and α-Mn phases, respectively. In the hot pressing process, the weight fraction of the MnBi phase decreases from 74.16% to 69.19%, whereas that of the Bi phase increases from 13.19% to 17.57%. However, the weight fractions of α-Mn in the LEBM powder and hot pressed MnBi bulk are less than about 12%.

Figure 2(a) shows the morphologies of the LEBM MnBi powder, while the microstructure of the fracture surface of the hot pressed MnBi bulk is shown in Fig. 2(b). The grain size of the MnBi bulk increased up to 10 μm in Fig. 2(b) from the LEBM MnBi powder ranging from 1 to 7 μm in Fig. 2(a) due to the high pressure and grain growth. Figure 2(c) is the Back-Scattered Electron (BSE) image of the MnBi bulk. The BSE image demonstrates that the melted and recrystallized Bi acts as a binder between MnBi particles during the hot pressing process. Increasing the content of the melted Bi, which occupied both weight and space in the MnBi bulk magnet, as shown in Fig. 2(c), results in the decreased magnetization. It can be found that there are several pores that are marked with black color in the image. The pores decrease both the density and magnetic properties of the bulk MnBi magnet. Figure 3 shows the magnetic hysteresis loops of the LEBM MnBi powder, aligned LEBM MnBi powder in paraffin, and MnBi bulk up to 40 kOe at room temperature. The detailed magnetic properties are listed in Table I. After the hot pressing process, the magnetization at 40 kOe (\(M_{40\text{kOe}}\)) increases from 37 to 49 emu/g, while \(H_c\) decreases from 8953 to 6272 Oe.

The density and \(H_c\) can be enhanced by filling the pores and grain boundaries in the MnBi bulk with diffusion materials or nanopowder. NaCl and C powders can easily be ground to nanosized powders. Therefore, we have mixed the manually ground coarse MnBi powder with the high energy ball milled nanosized NaCl or C powder and then LEBM for 4 h, which exhibited the highest \(H_c\) in the pure MnBi powder. The mixed powders were then used to produce MnBi/NaCl or MnBi/C bulk magnets in the same condition with the pure MnBi bulk.

Due to the low content of NaCl or carbon, the NaCl or carbon phase cannot be clearly observed in the XRD patterns in Fig. 4. Therefore, to clearly analyze the phase identity, we have analyzed by using the Rietveld refinement method. The resulting Bragg factor (\(R_B\)) and structure factor (\(R_F\)) were all less than 5%. From the refined XRD patterns, the peak of NaCl could be slightly observed because of the better crystallinity than C. With increasing content of NaCl or C, the nonmagnetic Bi peaks in the XRD patterns were increased due to phase decomposition of LTP MnBi, leading to decreased \(M_{40\text{kOe}}\). Theoretical densities of NaCl and C are 2.16 and 2.25 g/cc, respectively, which are much lower than the theoretical density of LTP MnBi, i.e., 8.9 g/cc. Therefore, the densities of the bulk magnets were decreased with the increasing NaCl or C content, as listed in Table II.

Figure 5 shows the magnetic hysteresis loops of the MnBi bulks with NaCl or C of 2 and 5 wt. %, and the detailed...
Refined XRD patterns of the MnBi/NaCl and MnBi/C bulks are shown in FIG. 4. The magnetic properties are summarized in Table I. With increasing C or NaCl content, $H_c$ of the MnBi bulks were significantly increased. This is because the NaCl or C particles fill the pores and separate the MnBi grains in the MnBi bulks and act as pinning centers for the domain walls by strongly inhibiting their motion, thus reducing the efficiency of the reversal mechanism. On the other hand, the increasing NaCl or C content degrades $M$ of the MnBi bulk magnets due to increasing content of nonmagnetic phases.

### Table II. Densities of the MnBi, MnBi/NaCl, and MnBi/C bulks.

| Sample          | Density (g/cc) |
|-----------------|----------------|
| Pure MnBi       | 8.08           |
| C (2 wt. %)     | 6.67           |
| C (5 wt. %)     | 7.34           |
| NaCl (2 wt. %)  | 6.80           |
| NaCl (5 wt. %)  | 6.98           |
IV. CONCLUSIONS

MnBi bulk magnetic materials were successfully fabricated by hot pressing, and their crystallographic and magnetic properties were analyzed. The MnBi bulk magnets with enhanced coercivities have been produced by hot pressing of low energy ball milled powder mixtures of MnBi and NaCl or C powders. A small addition of NaCl and C in the MnBi bulks acts as pinning centers for domain wall motions. The coercivity ($H_c$) of the MnBi bulks with NaCl of 5 wt. % and C of 5 wt. % reach 9041 Oe and 7054 Oe, respectively, which are higher than the pure MnBi bulk of 6272 Oe. Therefore, the proper addition of NaCl or C into the grain boundaries of MnBi bulks is thought to be a promising route to enhance the magnetic properties of the MnBi bulk magnetic materials.

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