2019

High energy product of MnBi by field annealing and Sn alloying

Wenyong Zhang
Balamurugan Balasubramanian
Parashu Kharel
Rabindra Pahari
Shah R. Valloppilly

See next page for additional authors

Follow this and additional works at: https://digitalcommons.unl.edu/cmrafacpub

Part of the Atomic, Molecular and Optical Physics Commons, Condensed Matter Physics Commons, Engineering Physics Commons, and the Other Physics Commons

This Article is brought to you for free and open access by the Materials and Nanoscience, Nebraska Center for (NCMN) at DigitalCommons@University of Nebraska - Lincoln. It has been accepted for inclusion in Faculty Publications from Nebraska Center for Materials and Nanoscience by an authorized administrator of DigitalCommons@University of Nebraska - Lincoln.
Authors
Wenyong Zhang, Balamurugan Balasubramanian, Parashu Kharel, Rabindra Pahari, Shah R. Valloppilly, Xingzhong Li, Lanping Yue, Ralph Skomski, and David J. Sellmyer
High energy product of MnBi by field annealing and Sn alloying

Cite as: APL Mater. 7, 121111 (2019); doi: 10.1063/1.5128659
Submitted: 20 September 2019 • Accepted: 6 December 2019 • Published Online: 23 December 2019

Wenyong Zhang,1,2,a) Balamurugan Balasubramanian,1,2 Parashu Kharel,1,3 Rabindra Pahari,1,2 Shah R. Valloppilly,1 Xingzhong Li,1 Lanping Yue,1 Ralph Skomski,1,2 and David J. Sellmyer1,2

AFFILIATIONS
1 Nebraska Center for Materials and Nanoscience, University of Nebraska, Lincoln, Nebraska 68588, USA
2 Department of Physics and Astronomy, University of Nebraska, Lincoln, Nebraska 68588, USA
3 Department of Physics, South Dakota State University, Brookings, South Dakota 57007, USA

a) E-mail: wenyong.zhang@unl.edu

ABSTRACT
Permanent-magnet materials are one cornerstone of today’s technology, abundant in disk drives, motors, medical equipment, wind generators, and cars. A continuing challenge has been to reconcile high permanent-magnet performance with low raw-material costs. This work reports a Mn-Bi-Sn alloy exclusively made from inexpensive elements, exhibiting high values of Curie temperature, magnetization, anisotropy, coercivity, and energy product. The samples are produced by field annealing of rapidly quenched Sn-containing MnBi alloys, where the improvement of the magnetic properties is caused by the substitutional occupancy of the 2c sites in the hexagonal NiAs structure by Sn. The substitution modifies the electronic structure of the compound and enhances the magnetocrystalline anisotropy, thereby improving the coercivity of the compound. The energy product reaches 114 kJ/m³ (14.3 MGOe) at room temperature and 86 kJ/m³ (10.8 MGOe) at 200 °C; this value is similar to that of the Dy-free Nd₂Fe₁₄B and exceeds that of other rare-earth-free permanent-magnet bulk alloys, as encountered in automotive applications.

© 2019 Author(s). All article content, except where otherwise noted, is licensed under a Creative Commons Attribution (CC BY) license (http://creativecommons.org/licenses/by/4.0/). https://doi.org/10.1063/1.5128659

Permanent magnets require not only a high saturation magnetization \( M_s \) and a high Curie temperature \( T_C \) but also a high coercivity \( H_C \). Magnetization and coercivity largely determine the energy product \((BH)_{\text{max}}\) of a permanent magnet, a key figure of merit that describes the magnet’s ability to store magnetostatic energy in free space. While the energy product never exceeds \( J_s^2/4 \) (\( J_s = \mu_0 M_s \) is the saturation magnetic polarization), the main limitation is usually the coercivity. A key question is therefore the improvement of coercivity by enhancing the magnetocrystalline anisotropy and by creating a microstructure that prevents magnetization reversal in small reverse magnetic fields. It is relatively easy to ensure appreciable magnetizations and Curie temperature by using 3d elements such as Fe and Co, but high anisotropies tend to require expensive and/or supply-threatened elements such as rare earths and Pt. Cobalt, used, for example, in SmCo₅, is a special case: it is more expensive than Fe or Mn and exhibits industrially disadvantageous price fluctuations. Today’s leading room-temperature high-performance permanent magnets are made from the fairly expensive alloy Nd₂Fe₁₄B. Furthermore, powerful Nd-Fe-B motors, for example, in automotive applications, operate at temperatures of up to 200 °C. The anisotropy of Nd₂Fe₁₄B strongly decreases with increasing temperature, which is compensated by the addition of Dy, an expensive rare-earth element.

MnBi was discovered in 1904 as a by-product of the original research on Heusler alloys and later shown to crystallize in the hexagonal NiAs structure (space group \( P6_3/mmc \)), as shown in Fig. 1. Alongside other rare-earth-free materials, MnBi has long been considered as a potential permanent-magnet material since it contains neither rare earths nor expensive elements such as Ga and Pt. The magnetic-ordering temperature of MnBi, 377 °C, is higher than that of Nd₂Fe₁₄B (312 °C), the saturation magnetic polarization of \( J_s \approx 0.85 \) T is appreciable, and its anisotropy exhibits the unusual advantage of increasing with temperature.
However, the structure of MnBi is nontrivial, the ordering or Curie temperature actually is being a phase-transformation from a low-temperature phase (LTP) to a high-temperature phase (HTP), and its room-temperature magnetocrystalline anisotropy of 1.2 MJ/m³ is relatively low.

Based on density-functional calculations, Sakuma et al. suggested that the addition of Sn improves the anisotropy of MnBi. In their calculation, Sn occupies the 2c sites in the NiAs structure (Fig. 1), in agreement with the experimental situation in alloys of iron-series transition-metals and heavy metalloids. Sn is nonmagnetic, it affects the magnetic anisotropy of the Mn sublattice through crystal-field or "ligand-field" interactions. While Bi and Sn are nonmagnetic, they affect the magnetic anisotropy of the Mn sublattice through crystal-field or "ligand-field" interactions. The anisotropy is modified by Sn addition and supplemented by optimizing the microstructure through annealing in high magnetic fields. Empirical annealing procedures, which are common in permanent-magnet processing, have multiple purposes and require material-specific adjustments. In the present case, they control the magnetic anisotropy of the MnBi grains is parallel to the length of the ribbons. We have also carried out tilt-angle x-ray diffraction measurements, and the data clearly demonstrate that a significant grain reorientation is achieved with the c-axis aligned nearly parallel to the ribbon plane (along the length of the ribbon), within 10°–15° from the surface (Fig. S1 of the supplementary material).

We have used the Williamson Hall method to determine the crystallite size and microstrain in the annealed samples (Fig. S2 of the supplementary material). In our experiments, we have focused on simultaneously improving the anisotropy, coercivity, and energy product of MnBi. The anisotropy is modified by Sn addition and supplemented by optimizing the microstructure through annealing in high magnetic fields. Empirical annealing procedures, which are common in permanent-magnet processing, have multiple purposes and require material-specific adjustments. In the present case, they control the magnetic anisotropy of the MnBi grains is parallel to the length of the ribbons. We have also carried out tilt-angle x-ray diffraction measurements, and the data clearly demonstrate that a significant grain reorientation is achieved with the c-axis aligned nearly parallel to the ribbon plane (along the length of the ribbon), within 10°–15° from the surface (Fig. S1 of the supplementary material).

We have used the Williamson Hall method to determine the crystallite size and microstrain in the annealed samples (Fig. S2 of the supplementary material). In our experiments, we have focused on simultaneously improving the anisotropy, coercivity, and energy product of MnBi. The anisotropy is modified by Sn addition and supplemented by optimizing the microstructure through annealing in high magnetic fields. Empirical annealing procedures, which are common in permanent-magnet processing, have multiple purposes and require material-specific adjustments. In the present case, they control the magnetic anisotropy of the MnBi grains is parallel to the length of the ribbons. We have also carried out tilt-angle x-ray diffraction measurements, and the data clearly demonstrate that a significant grain reorientation is achieved with the c-axis aligned nearly parallel to the ribbon plane (along the length of the ribbon), within 10°–15° from the surface (Fig. S1 of the supplementary material).

We have used the Williamson Hall method to determine the crystallite size and microstrain in the annealed samples (Fig. S2 of the supplementary material). In our experiments, we have focused on simultaneously improving the anisotropy, coercivity, and energy product of MnBi. The anisotropy is modified by Sn addition and supplemented by optimizing the microstructure through annealing in high magnetic fields. Empirical annealing procedures, which are common in permanent-magnet processing, have multiple purposes and require material-specific adjustments. In the present case, they control the magnetic anisotropy of the MnBi grains is parallel to the length of the ribbons. We have also carried out tilt-angle x-ray diffraction measurements, and the data clearly demonstrate that a significant grain reorientation is achieved with the c-axis aligned nearly parallel to the ribbon plane (along the length of the ribbon), within 10°–15° from the surface (Fig. S1 of the supplementary material).
the supplementary material). This analysis yields negligibly small microstrain (≤0.04%) in the annealed MnBi and Sn-substituted MnBi samples. The average crystallite sizes are determined as 59 ± 7 nm (MnBi) and 62 ± 4 nm (MnBi0.9Sn0.1) for the annealed samples in the zero field. The crystallite-size values for the annealed samples in the magnetic field are 44 ± 2 nm (MnBi) and 42 ± 5 nm (MnBi0.9Sn0.1), and the result shows a reduction of about 30% crystallite size upon field annealing.

Figure 3(a) shows the temperature dependences of the magnetic polarization, \( J = \mu_0 M \), for the MnBi and MnBi0.9Sn0.1 ribbons annealed at 2 T and measured in a field \( B_0 = \mu_0 H = 0.1 \) T applied along the ribbon length. The \( J(T) \) curves show two clear transitions, a low-temperature spin-reorientation transition where the easy magnetization axis flips from the basal plane (\( a-b \) plane) to the \( c \)-axis and a high-temperature structural transition from ferromagnetic LTP MnBi to the paramagnetic HTP MnBi. The \( df/dT \) curves, Fig. 3(b), show that the temperatures of the spin-reorientation transition (\( T_a \)) and of the structural transition (\( T_c \)) slightly decrease on Sn doping. The slight decrease in \( T_c \) due to Sn doping is consistent with the theoretical predictions by Sakuma et al.

Figures 4(a) and 4(b) show the hysteresis loops of the field-annealed samples measured at room temperature (a) and at 200°C (b) along the easy-axis direction (the measurement field being applied along the ribbon length). We find that the saturation magnetic polarization \( J_s \) of the Sn-doped ribbons is slightly lower than that of pure MnBi at 300 K (Fig. S3 of the supplementary material), which agrees with the theoretical predictions. However, this effect is overcompensated by the enhanced remanence \( J_r \), as evidenced by the improved loop squareness of the Sn-doped samples (Fig. S4 of the supplementary material). The remanence ratios \( J_r/J_s \) of both MnBi and MnBi0.9Sn0.1 ribbons systematically increase with the annealing field, reaching almost 1 for the annealing field of 4 T (not shown here).

Figure 4(c) plots the room-temperature coercivity \( (B_c = \mu_0 H_c) \) and energy product as a function of the annealing field (c) and Sucksmith-Thomson plots at 300 K for the samples annealed at 4 T (d). The room-temperature coercivity of MnBi0.9Sn0.1 is significantly higher than that of MnBi, which is consistent with the increase in \( K \) measured for MnBi0.9Sn0.1 in the present study and theoretically predicted enhancement of the magnetocrystalline anisotropy. However, microstructural changes caused by annealing, such as grain-size refinement shown by XRD analysis and a possible pinning mechanism at grain boundaries, may also play a role in improving the coercivities in the Sn-substituted samples. Therefore, it is likely that the enhanced coercivity in MnBi0.9Sn0.1 reflects the increase in anisotropy, complemented by microstructural refinement through annealing. At 200°C, the effect of Sn lowers the coercivity because the thermal effect was not considered by Sakuma et al. However, the energy product remains high because of good loop squareness.

The maximum room-temperature energy product \( (BH)_{\text{max}} \) is equal to 114 kJ/m\(^3\) for the MnBi0.9Sn0.1 sample annealed at 4 T, compared to 67 kJ/m\(^3\) previously achieved in microcrystalline MnBi. Various types of Sm-Co and Nd-Fe-B magnets clearly exceed this threshold (see, e.g., Table A 4 in Ref. 9), but they contain expensive elements. Room-temperature MnBi energy products as high as 130 kJ/m\(^3\) have been achieved in textured thin films of MnBi on glass substrates, but these structures are generally not suitable for industrial applications. By contrast, melt spinning can be realized on an industrial scale, as exemplified by bonded Nd12Fe14B magnets. At 200°C, the energy product
of MnBi$_{0.9}$Sn$_{0.1}$ is 86 kJ/m$^3$, similar to that of Dy-free Nd$_2$Fe$_{14}$B and higher than that of other rare-earth-free bulk alloys.$^{16}$

There are two reasons for the present improvement, namely, the high volume fraction of the hard phase (no grain boundary phase) and the better c-axis alignment of the grains. Previously investigated MnBi-based magnets are nearly isotropic and exhibit lower coercivities and energy products.$^{20,25,26,40}$ The formation of a Bi grain boundary phase, which helps to develop coercivity, also limits the energy product because Bi is nonmagnetic. By comparison, Sn replaces Bi in MnBi and does not therefore significantly reduce magnetization. Recent research on alloying MnBi with elements including Sn, Sb, and Mg$^{41–44}$ has been shown to increase the coercivity and energy product. In particular, a maximum energy product of 92 kJ/m$^3$ has been obtained in a compacted magnet with a nominal composition of Mn$_{50}$Bi$_{45}$Mg$_{5}$Sb$_{0.5}$. It may also be possible to produce bulk magnets using magnetically aligned MnBi$_{0.9}$Sn$_{0.1}$ ribbons by following the standard processing method used to fabricate bonded magnets.$^{45}$ That is, bulk MnBi$_{0.9}$Sn$_{0.1}$ may be fabricated by crushing the ribbons into micrometer-sized powder, mixing the particles homogeneously using epoxy resin, and solidifying them in a magnetic field of 1–3 T. Such processing studies remain for the future.

In conclusion, we have developed a new processing method and produced MnBi with a high room-temperature energy product of 114 kJ/m$^3$. The energy-product improvement has been achieved by high-field annealing in combination with Sn substitution for Bi. Our alloy can be regarded as a low-cost high-performance permanent-magnet material for applications that require energy products between mass-produced cheap ferrite magnets and expensive high-performance rare-earth magnets. The melt-spin ribbons may be further processed to create bulk magnets by milling and polymer or metal bonding, similar to bonded ferrite or Nd-Fe-B magnets.

See the supplementary material for the additional figures, analysis, and discussion.

This work was supported by the Department of Energy/Basic Energy Science (Grant No. DE-FG02-04ER46152) and performed in part in the Nebraska Nanoscale Facility: National Nanotechnology Coordinated Infrastructure and the Nebraska Center for Materials and Nanoscience, which are supported by the National Science Foundation (Grant No. NNCI-1542182) and the Nebraska Research Initiative.