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Anisotropic nanocrystalline MnBi with high coercivity at high temperature

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Magnetic hard nanocrystalline MnBi has been prepared by melt spinning and subsequent low temperature annealing. A coercivity of 2.5 T can be achieved at 540 K for MnBi with an average grain size of about 20-30 nm. The coercivity iH_c, mainly controlled by the coherent magnetization rotation, shows a strong dependence on the time of grinding and exhibits a positive temperature coefficient from 100 up to 540 K. The unique temperature dependent behavior of the coercivity (magnetocrystalline anisotropy) has a relationship with the variations in the crystal lattice ratio of c/a with temperatures. In addition, discontinuity can not be found in the lattice parameters of a, c, and c/a ratio at the magnetostructural transition temperature. The nanocrystalline MnBi powder fixed in an epoxy resin and under an applied magnetic field of 24 kOe shows a maximum energy product of 7.1 MGOe at room temperature and shows anisotropic characteristics with high Mr/Ms ratio up to 560 K. © *2011 American Institute of Physics*. [doi:10.1063/1.3630001]

The intermetallic ferromagnetic compound MnBi has attracted much attention because of its high uniaxial magnetic anisotropy, high magneto-optical Kerr effect, and high spin polarization at room temperature.[1–13] For instance, the low temperature (LTP) phase with NiAs-type hexagonal crystal structure has a magnetic anisotropy energy of 2×10^7 erg/cm^3 at 500 K.[1] Upon heating to 628 K, a first-order magnetostructural transition takes place, corresponding to a phase decomposition of MnBi into $Mn_{1.08}Bi$ and free Bi with a 4% decrease in the hexagonal c/a ratio.[2] In addition, the magnetic hard LTP MnBi exhibits a positive temperature coefficient for coercivity, which is unique in magnetic materials.[1,3,4] High coercivity of 17 kOe at room temperature (RT) was found in nanostructured MnBi/Bi composites,[5,6] Its high temperature phase exhibits a high polar Kerr rotation of 1.25°.[7–9] Recently, a spin polarization of 63% has also been observed for MnBi with a large magnetoresistance.[10,11] Despite these improvements, the application of LTP MnBi, however, has been limited by conventional synthesis methods such as arc-melting and sintering that failed to get MnBi in a single phase. High purity or increased coervicity of LTB MnBi ribbons could be obtained by melt spinning.[3,12] But MnBi with both high saturation and coercivity has not been achieved by this approach. Since the magnetic properties of magnets are associated with phases, compositions, and microstructures of compounds, a detailed study of the structures and magnetic properties is required to improve the magnetic properties of MnBi. In this letter, we prepared high quality MnBi ribbons with nanocrystaline grains by melt spinning. The coercivity of nanocrystalline MnBi was found to be mainly controlled by the coherent magnetization rotation. A maximum energy product $(BH)_{max}$ of 7.1 MGOe was achieved at RT. The neutron diffraction was used to study the structure and phase transition of MnBi at various temperatures. It was found that the unique changes of anisotropy and coercivity are related to differences in crystal lattice parameters varied with temperatures.

MnBi ingots were prepared by arc-melting with high purity manganese (99.99%) and bismuth (99.99%) in suitable atomic ratios. The ribbons of MnBi were obtained by ejecting the melt of ingot from a quartz tube onto the surface of a rotating copper wheel under the argon atmosphere. The tangential speed of the wheel was in the range from 10 to 70 m/s. The ribbons were annealed at various temperatures in order to prepare MnBi with optimal magnetic properties. The obtained samples were grinded into powders, mixed with epoxy resin, and aligned in a magnetic field of 1.5 T. The volumetric and gravimetric ratios of the magnetic powders to the epoxy resin are about 3/50 and 1/3, respectively, which ensure a good alignment of the powders under the magnetic field. The density of the specimen was estimated to be 7.8 g/cm^3 using the lattice parameters and the molecular weight of MnBi. The structure of MnBi was studied by x-ray diffraction (XRD), neutron diffraction (ND), and transmission electron microscopy (TEM). Magnetic properties were measured using vibrating sample magnetometer and superconductivity quantum interference device.

In order to obtain high purity of LTP MnBi, Mn_xBi with various nominal compositions ($x = 0.9$–2.33) were synthesized and investigated. Fig. 1 shows the typical XRD patterns of Mn_xBi ($x = 1.22$). The amorphous ribbons were achieved using this rotation speed (Fig. 1(a)). Thus, Mn and Bi atoms can be homogeneously mixed, making them easier to form MnBi after the annealing. High purity of MnBi phase was found with $x = 1.20$–1.22 (Fig. 1(b)). Large amount of

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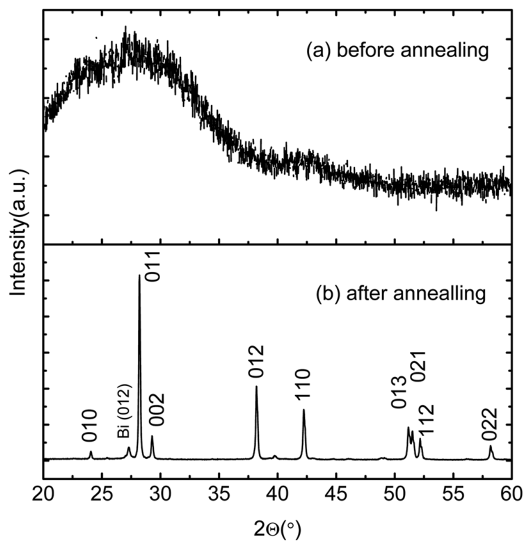

FIG. 1. XRD patterns of the MnBi after melt spinning at a speed of 65 m/s (a) and subsequently annealed at 573 K for 3 h (b).

Bi phase appears if Mn content is less than 1.1, while Mn and MnO_2 phases appear if Mn content is too high in the composition as shown in the XRD pattern of $Mn_{2.33}Bi$. After refinement of the neutron diffraction data of the high purity MnBi, the room temperature lattice parameters of a = 4.2854, c = 6.1229 Å with hexagonal symmetry were obtained. The observed content of MnBi is higher than 95%, and Mn shows a magnetic moment of 3.6μ_B per atom. The measured magnetization of MnBi sample is about 75 emu/g at 7 T, very close to its theoretical saturation magnetization value of 80 emu/g at room temperature, confirming that high purity of the sample can be achieved with a quenching speed of 65 m/s.

The TEM images of the annealed MnBi with various quenching speeds are shown in Fig. 2. Well shaped hexagonal MnBi single crystal grains with an average size of 200 nm are observed in the samples with a speed of 20 m/s (Fig. 2(a)). Those single crystal-like grains are crystallographically oriented along the c-axis of the MnBi according to the electron diffraction patterns, which shows typical hexagonal spot pattern along the [001] direction (see Fig. 2(b)). This orientation is critical to form anisotropic magnetic powders. However, the average grain size decreases to about 20–30 nm when a quenching speed of 65 m/s is applied (see high resolution lattice image Fig. 2(c)).

In order to improve the magnetic properties, the annealed ribbons were grinded for various lengths of time. It is found that the coercivity increases with the length of grinding time and reaches a value of 1.1 T at RT. The decoupling between hard magnetic grains may account for the coercivity change. Interestingly, the increase of the coercive field is accompanied with slight decrease of the saturation magnetization and remanence. In order to avoid the oxidization of the powders, MnBi was grinded in a mortar protected by petroleum ether. The oxygen content in the MnBi powders was monitored. The oxygen content is about 0.15 wt. % after grinding of 5 min and is about 1.1 wt. % after grinding of 7 h. The maximum energy product at RT is about 7.1 MGOe after 7-h grinding. The corresponding hysteresis loop of MnBi is plotted in Figure 3(a) and a very high Mr/Ms > 90% is obtained. Since most nanocrystalline compounds prepared by melt spinning is isotropic and has a Mr/Ms ratio of normally less than 60%, such a high Mr/Ms ratio of nanocrystalline MnBi is unique and the crystallographically orientation of the single crystal grains is likely to be the cause. In addition, the grain size of the above MnBi magnet is about 20–30 nm, much less than that of a single domain size of 250 nm. Thus, the magnetization reversal may be associated with the magnetization rotation controlled

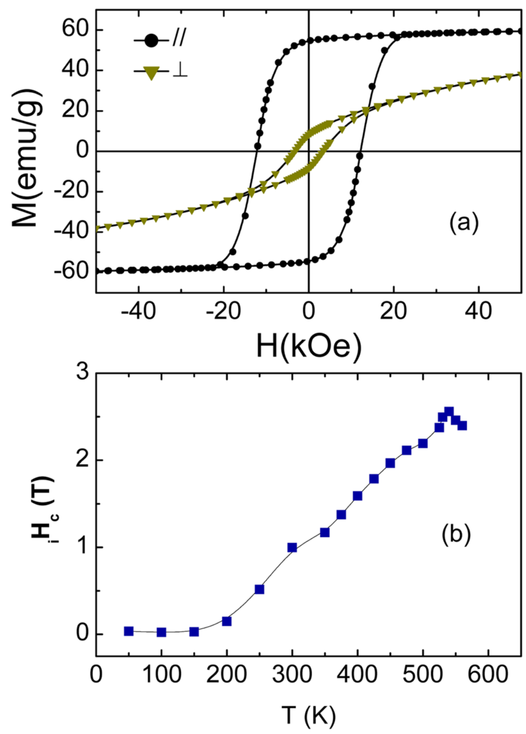

FIG. 3. (Color online) The magnetic properties of MnBi. The hysteresis loop of MnBi at RT (a), the temperature dependence of coercivity for nanocrystalline MnBi (b).

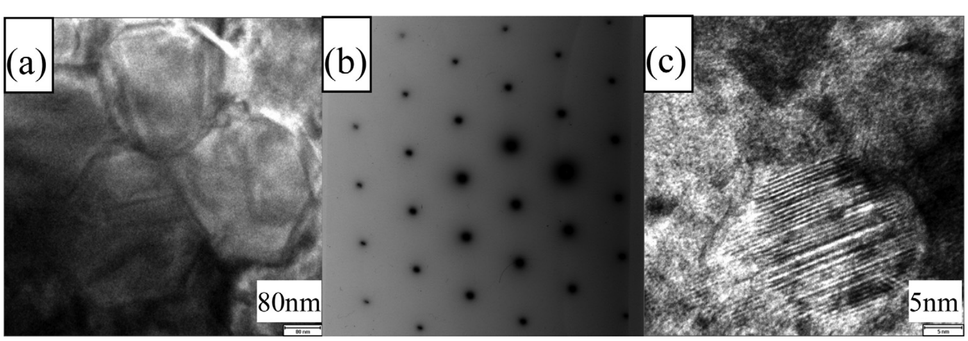

FIG. 2. TEM images of the annealed MnBi with quenching speed, 20 m/s (a), the electron diffraction pattern of MnBi grains (b), and the TEM images of annealed MnBi with quenching speed of 65 m/s (c).

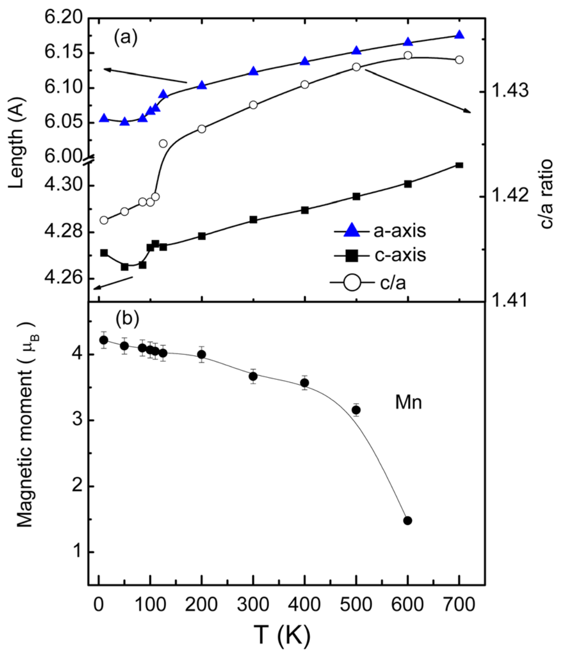

FIG. 4. (Color online) The lattice parameters a, c and c/a ratio of MnBi at different temperatures (a), and the temperature dependence of the Mn magnetic moment in MnBi (b).

by magnetocrystalline anisotropy.[14] The domain wall pinning is probably not the dominant mechanism since no domain wall nucleates can be produced during the coherent magnetization reversal. In order to identify the magnetization reversal mechanism for MnBi nanocrystalline materials, the angular dependence of coercivity is obtained from the hysteresis loops measured at various angles. The coercivity decreases with the increasing angle between the easy axis and the applied field direction, indicating that a coherent rotation of magnetization occurs in MnBi according to the classical Stoner–Wohlfarth model.[15] The field dependence of the coercivity further supports this finding. The temperature dependence of the coercivity is shown in Fig. 3(b), which exhibits a positive temperature coefficient. The coercivity of MnBi increases with the temperature from 100 to 540 K, and reaches a maximum of 2.5 T at 540 K. The positive temperature coefficient of the coercivity may have some relationship with the magnetocrystalline anisotropy field of MnBi. From 150 K to 530 K, the anisotropy field increases with temperature and reaches the maximum at 530 K.[3]

In order to have a better understanding of the mechanism of this phenomenon, ND was performed to study the phase and composition evolution of MnBi with various temperatures. Fig. 4 is the temperature dependence of lattice parameters and magnetic moments of MnBi obtained from refined ND data. A kink is observed around 100 K in both a and c axes, suggesting a spin reorientation of the Mn atoms.[3,16,17] The relaxation of the lattice is found to be associated with changes in the magnetocrystalline anisotropy from planar to c-axis. When the c/a ratio is less than 1.425, the LTP MnBi shows planar anisotropy; as $c/a > 1.425$, the uniaxial anisotropy appears and the anisotropic field increases with the increase of c/a up to 1.433. When the c/a ratio reaches 1.433, a magnetostructural phase transition from ferromagnetic to paramagnetic occurs (See Fig. 4(a)). At the magnetostructural transition, the c/a ratio of the nanostructured MnBi remains unchanged whereas that of the bulk material decreases abruptly to 1.37.[2] Similar to MnBi nanorods in the Bi matrix,[16] no evidence of discontinuity is noticed for the lattice a- and c-parameters at 625 K for high purity nanocrystalline MnBi, while the discontinuity is easily seen in the lattice parameters of the bulk at this temperature.[2] The magnetic moment of Mn atom decreases slowly with increase of the temperature (Fig. 4(b)) and shows no discontinuity around 100 K corresponding to the spin reorientation of the Mn atom. A sharp drop of the magnetic moment was observed at 540–550 K due to the magnetic phase transition, and it reaches a value of 1.4 μ_B at 600 K.

In conclusion, we report that over 95 wt. % nanocrystalline LTP MnBi can be prepared by melt spinning. The average size of MnBi grains is 20–30 nm, much smaller than the single domain size of 250 nm. Coercivity H_c can be greatly improved by grinding and a positive temperature coefficient is observed. The maximum energy product $(BH)_{max}$ of the magnet is about 7.1 MGOe at room temperature. The magnetic anisotropy changes from planar to uniaxial with the changes of the c/a ratio, which may contribute to the unique temperature coefficient of the coercivity of MnBi.

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