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Temperature dependences of structure and coercivity for melt-spun MnBi compound

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ABSTRACT

Low temperature phase MnBi compound was prepared by annealing the melt-spun amorphous MnBi ribbons. Temperature dependences of structure, magnetization and coercivity were investigated using neutron/X-ray powder diffraction and magnetic measurements. It is found that the lattice parameter c/a ratio of the MnBi increases with the increasing temperature and finally reaches a maximum of 1.433 around 600 K. No structural phase transition is observed at 633 K. Especially, the lattice constants of MnBi at 700 K are $a=b=4.30919$ Å, and $c=6.17521$ Å, which are not in accordance with the previous data for bulk MnBi. Magnetic moment of Mn atom tends to lie in the ab-plane at 10 K, and turns to align along c-axis around 90 K. The growth of LTP MnBi grains is observed above 500 K, which increases the content of MnBi. The coercivity of MnBi shows a positive temperature coefficient, reaches a maximum of 2.5 T at 540 K, and decreases to 1.8 T at 610 K. The temperature dependence of the coercivity is related to the change of magnetocrystalline anisotropy, and shows strong dependence on the sizes of MnBi particles.

1. Introduction

The low temperature phase (LTP) MnBi compound is of current interest due to its magnetic properties [1–3]. It shows large magnetic moments of 3.6 Bohr magnetons for Mn atoms [2,3], and simultaneously possesses high uniaxial magnetic anisotropy (the anisotropy constant $K=1.6\times10^6$ J/m^3) [4,5] at 300 K. For oriented single domain particles, the coercivity expected from $2K/I_s$ is about 50000 Oe. (I_s is the saturation magnetization.) Especially, the structure and magnetic properties of LTP MnBi from 300–700 K are the most attractive. Firstly, the coercivity $_iH_c$ of the LTP MnBi shows a positive temperature coefficient from 150 K to 550 K [6,7], which makes it very favorable for high temperature applications. Secondly, the latest reports found that MnBi nanorods [8] show unusual lattice-magnetism connections at high temperature, suggesting the possibility to tailor the magnetic properties at high temperature. Up to now, the origin of the positive temperature coefficient for coercivity is not clear, mainly because of the lack of structure and magnetic property measurements at high temperature. The initial structural research of MnBi can be traced to the work of Andersen et al. [9] in 1967 who reported the neutron diffraction patterns of MnBi around the phase transition temperature of 633 K. After that, no similar neutron diffraction (ND) patterns are repeated. In this work, high purity MnBi has been prepared by melt spinning and subsequent annealing. The structure of the sample was investigated at different temperatures by neutron/X-ray diffraction (XRD) techniques. The magnetic properties at high temperature were studied and a tight connection between the structure and magnetic properties was found.

2. Experimental details

Mn_xBi_{100-x} ingots were prepared by arc-melting with high purity manganese (99.99%) and bismuth (99.99%) in atomic ratios. The ingots were then divided equally into several parts with each part about 2.5 g. The ribbons of MnBi were obtained by ejecting the melt from a quartz tube onto the surface of a rotating copper wheel with different speeds under argon atmosphere. The ribbons were then annealed at different temperatures. XRD measurement was carried out by using an X'pert Pro MPD diffractometer with Cu-Kα radiation. The neutron diffraction patterns at different temperatures were measured using the high resolution powder diffractometer BT-1 at National Institute of Standards and Technology (NIST) center for Neutron Research

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(NCNR). Structural data were obtained by refining the ND patterns using the software FULLPROF with Rietveld method. For the measurements of hysteresis loops, the ribbons were ground into powders, mixed with epoxy resin and then aligned in a magnetic field of 1.5 T. The temperature dependences of magnetic properties of MnBi were measured with the physical properties measurement system (manufactured by Quantum Design, Inc.).

3. Results and discussion

3.1. Preparation of LTP MnBi

Mn_xBi_{100-x} ($50 \leq x \leq 70$) ingots were melt-spun with different speeds. XRD patterns indicated that the amorphous degree of the ribbons increases with the increasing speed. Amorphous MnBi can be achieved with a speed of 65 ms^{-1}. In order to get high purity LTP MnBi, appropriate annealing condition was determined with differential scanning calorimetry (DSC). Fig. 1(a) shows the DSC curve of the as-prepared amorphous ribbon taken at 10 K/min. The first exotherm, peaking at 415 K, is followed by an endotherm at 540 K. A second exotherm very close to the first endotherm is reported to be related to the formation of LTP MnBi [10]. There is also a third endotherm appearing at about 633 K which should be corresponding to a phase transition. Several annealing temperatures for the amorphous ribbons are chosen according to these peaks in DSC curve. The XRD patterns of the ribbons annealed at these temperatures are shown in Fig. 1(b). High purity MnBi compound could not be prepared at a temperature below 473 K. The ribbons after annealing at 473 K contained several phases, including Bi, MnBi and Mn_3Bi. Mn diffraction peaks were not detected because a part of Mn is volatilized or oxidized during arc-melting and melt-spinning processes. In addition, some of the Mn may still be in the amorphous state because the annealing temperature is too low. With increasing temperature, the formation process becomes much faster. The first endotherm peak at 540 K seems to be critical for the growth of MnBi compound. Therefore, LTP MnBi is best formed by annealing the melt-spun ribbons at a temperature of 573 K with a composition of $Mn_{55}Bi_{45}$. The ribbons annealed at 473 K contain little MnBi while those annealed at 723 K and 823 K decompose into Bi and α-Mn.

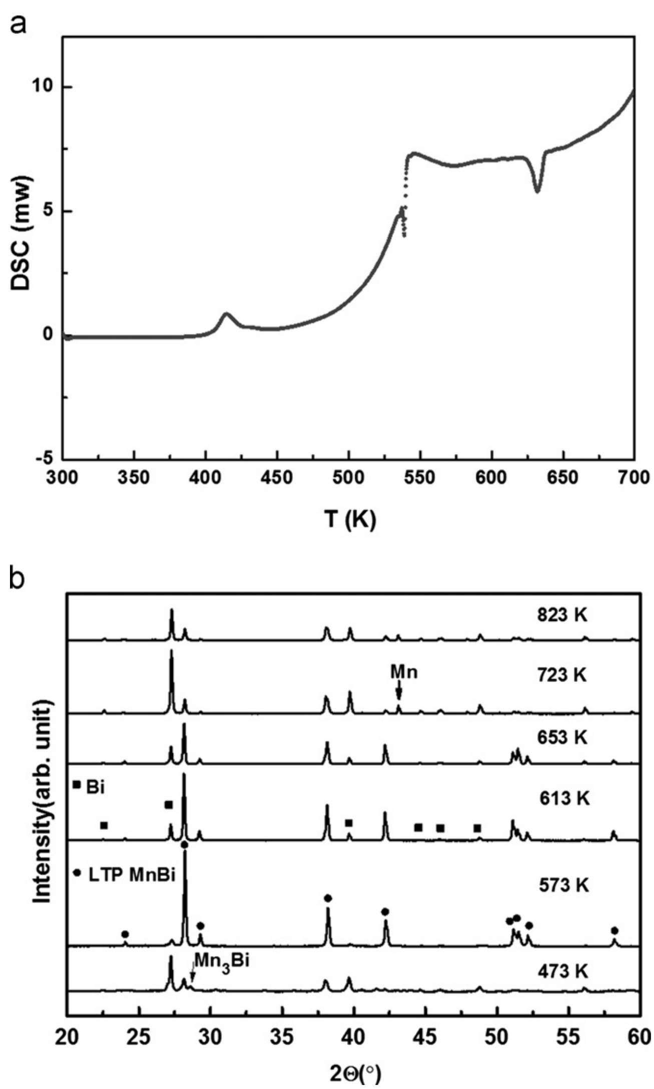

Fig. 1. (a) DSC scan of melt-spun MnBi ribbons with heating rate of 10 K/min. (b) XRD patterns, taken at room temperature, for the sample annealed at different temperatures.

3.2. Crystal and magnetic properties of MnBi at different temperatures

Fig. 2 shows the neutron diffraction patterns of MnBi measured at different temperatures. Bragg positions of phases were indicated under the patterns. All reflections of MnBi were labeled and reflections with major magnetic contribution were marked with M. The refinements of ND patterns were taken using the Rietveld method [11]. Magnetic structures with magnetic moments in spherical mode were adopted to determine the magnetic moments of Mn atoms. The purity of LTP MnBi is about 95 wt.% at 300 K. There is a little residual Bi phase in the sample. The phase of Al in the patterns comes from the container during measurement. Both of them can be distinguished from the patterns by the refinements. Weak manganese oxide impurity peaks were also observed in the high temperature patterns. The refined results are listed in Table 1. It is found that the lattice constants and unit cell volumes increase with the increasing temperature. The c/a lattice parameter ratio for MnBi reaches a maximum of 1.433 at about 600 K. The nearest Mn–Mn distances are in the range from 3.038 to 3.082 Å which is much larger than that in the elemental Mn (2.754 Å). The large Mn–Mn distance leads to the ferromagnetic coupling of Mn atoms according the Bethe–Slater curve [12].

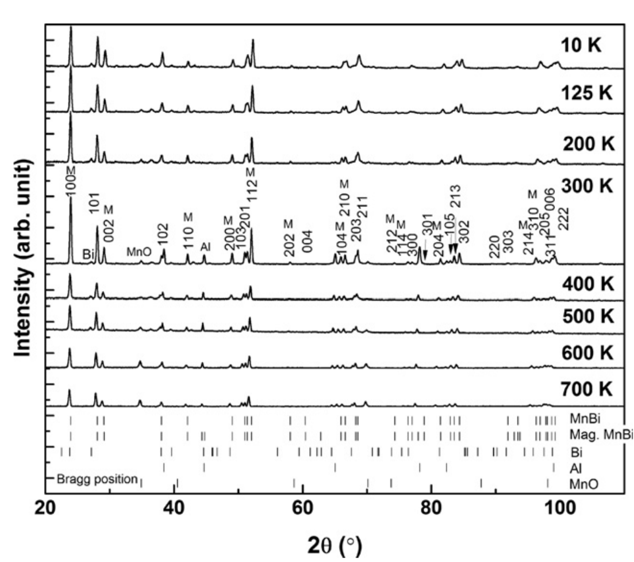

Fig. 2. ND patterns of LTP MnBi at different temperatures. The Bragg positions of MnBi, Bi, Al, and MnO are marked with vertical lines.