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Mn-Ga alloys have shown hard magnetic properties, even though these alloys contain no rare-earth metals. However, much work is needed before rare-earth magnets can be replaced. We have examined the magnetic properties of bulk alloys made with partial replacement of both the Mn and Ga elements in the $Mn_{0.8}Ga_{0.2}$ system. Bulk samples of Mn-Ga-Bi, Mn-Ga-Al, Mn-Fe-Ga and Mn-(FeB)-Ga alloys were fabricated and studied using mechanically milling and heat treatments while altering the atomic percentage of the third element between 2.5 and 20 at%. The ternary alloy exhibits all hard magnetic properties at room temperature with large coercivity. Annealed Mn-Ga-X bulk composites exhibit high coercivities up to 16.6 kOe and remanence up to 9.8 emu/g, that is increased by 115% over the binary system. [http://dx.doi.org/10.1063/1.4943931]

INTRODUCTION

Research in magnetism has long included the discovery and development of ever more powerful magnetic materials. This pursuit is motivated by the enduring challenge of progressively enhancing properties, such as the magnetization, while also grasping an understanding of the fundamental mechanisms behind those properties. Magnets have provided the backbone of many important products ranging from computers, to electric cars, and even wind-powered generators.[1] The novel class of rare-earth magnets containing neodymium has propelled permanent magnet research to its current plateau. Magnetic properties exceeding all previous values have been realized in Nd_2Fe_{14} B magnets.[2,3] However, researchers revealed that producers and their government will likely exercise tighter restrictions on rare earth ore exports and institute strict curbs on rare earth mines. This is due to the goal to control the reserves of rare earths in response to domestic economic priorities of the producer and an intention to clean up existing environmental issues related to past mining.[3] This has led to the search for a non-rare earth containing bulk material that will achieve similar magnetic strength and energy product as its rare earth counterpart.

Bulk Mn-Ga material has become a widely researched material in recent years.[4–11] Of the stable phases, the tetragonal Mn_3Ga with DO_{22} structure has gotten considerable attention because of the ferrimagnetic ordering,[12] high Curie temperature,[8,12–15] large magnetic anisotropy and high coercivity of exceeding 18 kOe in bulk materials.[4,6] Having a low remanent magnetization, M_r, and high coercivity, H_c, Mn_3Ga and other Mn-based magnets are good candidates for magnetic random access memory.[16] However, because of the low remanent and relatively high material cost, Mn_3Ga alone is not yet suitable for some permanent magnetic applications. An effective technique for increasing the magnetic properties is the addition or replacement with another element in the material. Altering the crystal symmetry, with the addition of a third element, can change the magnetocrystalline anisotropy of the material and improve the energy product of the material.

Substitutions on the Mn and on the Ga sites with small amounts of the other elements were examined. For the Ga site both Al and Bi were examined. Both elements have very different atomic radii from Ga (Al's radius is 13% smaller and Bi's radius is 5% larger) and have shown hard magnetic properties in binary compounds with Mn. The Mn was replaced with Fe and a mixture of Fe and B, which was added by a FeB compound. The iron was chosen due to the atomic radius of Fe is only 3% smaller than that of Mn, making it able to occupy the same site occupied by Mn in the unit cell. As Fe itself has ferromagnetic ordering, it is expected to enhance the magnetic moment in the system. The B atoms are expected to be interstitial atoms and are expected to add crystallographic anisotropy to the material by adding some crystal distortion. Researchers reported that Fe_xB_y type materials form soft magnetic materials with high magnetization.[17] We also hope that B and Fe can form soft magnetic component in the materials to enhance the remanence. In this study, we report our work on improvement of the remanence and overall magnetization by partial element substitution.

EXPERIMENTAL

Samples were prepared through a high energy ball milling process. Manganese powder (-325 mesh, 99.3%), solid gallium (99.999%) were loaded into a tungsten carbide mixing vial. For the substitution of the Ga site, either bismuth powder (-325 mesh, 99.5%) with a nominal chemistry of $Mn_{0.8}(Ga_{0.2-x}Bi_x)$ or aluminum powder (-325 mesh, 99.97%) with a nominal chemistry of $Mn_{0.8}$ $(Ga_{0.2-x}Al_x)$ with x=0.025 by atomic mass was added to the mixing vial. For samples with substitution of the Mn site either iron powder (-325 mesh, reduced, 98%) with a nominal chemistry $(Mn_{0.8-x}Fe_x)Ga_{0.2}$ or iron boride powder (-325 mesh, 98%) with a nominal chemistry of $(Mn_{0.8-x}(FeB)_x)Ga_{0.2}$ with x=0.05 by atomic mass was added to the mixing vial. The raw materials were milled for intermediate periods for a total time of 3 h in an argon environment in a high energy mill (SPEX 8000M). The milled powders were pressed, sealed in evacuated quartz tubes and heat treated for 2 h at temperatures ranging from 255 °C to 400 °C.

The crystallographic structure was determined by x-ray diffraction (XRD) taken at room temperature, using Cu Kα1 radiation. Magnetic properties were investigated by a vibrating sample magnetometer (VSM) in a physical property measurement system (PPMS) capable of fields up to 9 T (Quantum Design). Each sample was cut into an approximately cubic shape before magnetic testing to simplify geometrical demagnetization factors. The measurements were performed at room temperature.

RESULTS

The XRD diffraction patterns (Fig. 1) show multiple Mn and Mn-Ga phases in $Mn_{0.8}Ga_{0.2}$ type alloys doped with different elements. The major peaks show a phase prototype of $TiAl_3$ (similar to the ε-Mn_3Ga phase) with the tetragonal DO_{22} structure (space group: I4/mmm). The other two phases are α-Mn and cubic $Mn_{0.85}Ga_{0.15}$ with a phase prototype of high temperature β-Mn (space group: $P4_132$). We expect that Fe replaces Mn in our material and the Bi or Al replace the Ga. The major phases are identified as $(Mn,Fe)_3Ga$, $(Mn, Fe)_{0.85}Ga_{0.15}$ and α -Mn(Fe), B acts as interstitials in the material for the $(Mn_{0.8-x}(FeB)_x)Ga_{0.2}$ samples. The major phases are identified as $Mn_3(Ga,Bi)$, $Mn_{0.85}(Ga,Bi)_{0.15}$ and α –Mn for the $Mn_{0.8}(Ga_{0.2-x}Bi_x)$.

The M(H) hysteresis loops (Fig. 2) show hard magnetic properties in all the samples. Obvious shoulders are observed in the hysteresis loops, which may originate from incomplete coupling between ferromagnetic β-Mn ($Mn_{0.85}Ga_{0.15}$) and the ferrimagnetic ε phase (Mn_3Ga) in the samples. The magnetic properties samples with nominal chemistries of $Mn_{0.8}(Ga_{0.175}Al_{0.025})$ and $Mn_{0.8}(Ga_{0.175}Bi_{0.025})$ vary with of heat treatment temperatures (Fig. 3 & 4). At all the heat treatment temperatures, both ternary samples show hard magnetic properties, achieving high coercivities at optimized temperatures. The coercivity of samples with the addition of 2.5 at. % Al reaches a value of H_c = 9.6 kOe when annealed at 330 °C and samples with the addition of 2.5 at. % Bi reaches a value of H_c = 16.6 kOe when annealed at 315 °C. While these values are lower than

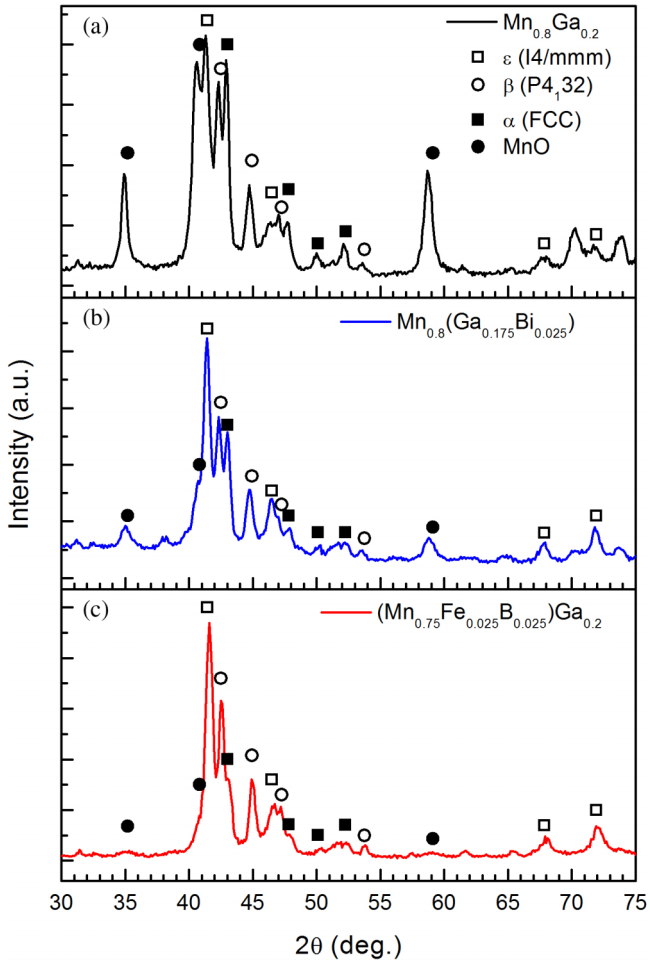

FIG. 1. Typical x-ray diffraction pattern of a (a) Mn0.8Ga0.2 sample annealed at 315 °C for 2 h, (b) $Mn_{0.8}(Ga_{0.2-x}Bi_x)$ sample with designated x=0.025 annealed at 310 °C for 2 h, and (c) $(Mn_{0.8-2x}Fe_xB_x)Ga_{0.2}$ sample with designated x=0.025 annealed at 360 °C for 2 h. All samples show a combination of two magnetic Mn-Ga phases, a non-magnetic Mn phase and a non-magnetic Mn oxide phase.

the binary system, the remanence, M_r, is greatly improved, especially in the system with the Bi addition. 2.5 at. % addition of Bi enhances the remanence in $Mn_{0.8}(Ga_{1-x}, B_x)_{0.2}$ samples annealed at 310 °C by 60 %, improving from 4.6 emu/g for $x = 0$ to 7.4 emu/g. The amount of Bi in the system was increased further in order to better understand how the third element affects the magnetic properties. When the Bi content is increased to 5 at. %, the magnetic properties dramatically drop off.

The magnetic properties of samples with nominal chemistries of $(Mn_{0.75}Fe_{0.05})Ga_{0.2}$ and $(Mn_{0.75}Fe_{0.025}B_{0.025})Ga_{0.2}$ change with heat treatment temperatures (Fig. 4). The remanence, M_r, is greatly improved by annealing at 360 °C, in the system with the both Fe and B additions. Both samples have hard magnetic properties, achieving high coercivities. The coercivity of samples with the addition of 5 at% Fe reaches a value of H_c = 13.8 kOe when annealed at 370 °C. The magnetic properties are optimized when addition of 2.5 at% Fe and 2.5 at% B is added and the sample is annealed at 360 °C. At this fabrication condition, coercivity reaches 15.3 kOe and remanence reaches 9.9 emu/g. The additions of 2.5 at. % of both Fe and B decreased the H_c by about 14 %, while it increased the remanence by more than 115 % from 4.6 emu/g for x=0. When both Fe and B contents reach 10 at. % the magnetic properties drastically drop off. This can be attributed to the soft magnetic nature of excessive FeB compound.

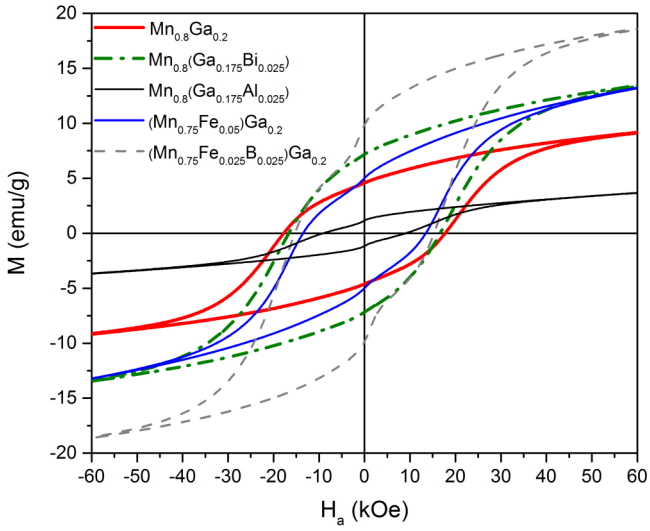

FIG. 2. Hysteresis loops of elemental replaced samples. All samples exhibit hard magnetic properties, featuring wide M (H) loops and a high coercivity.

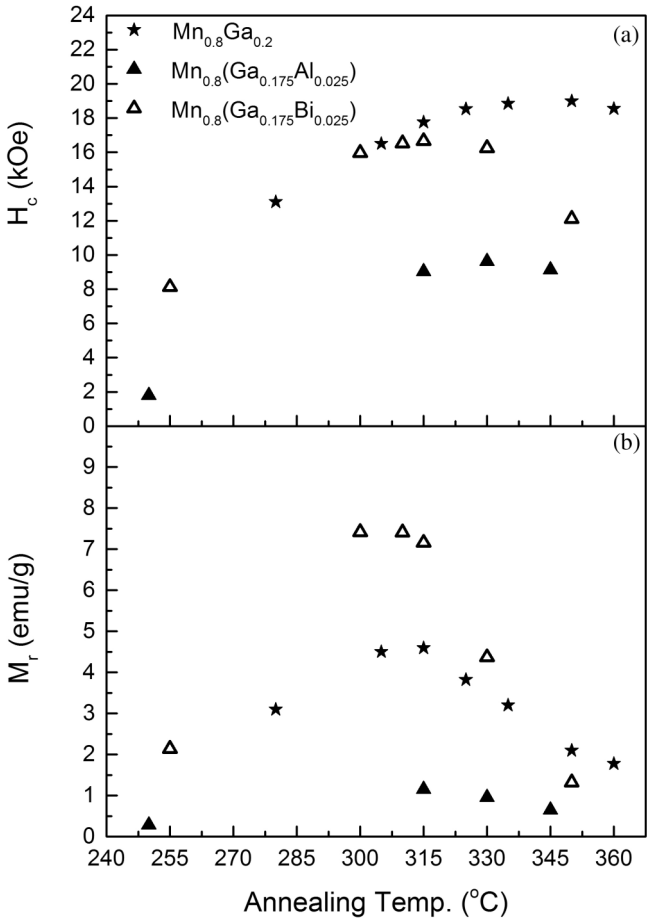

FIG. 3. (a) Coercivity, H_c, (b) remanence, M_r, of heat treated samples containing 2.5 at.% of a third element in place of Ga.

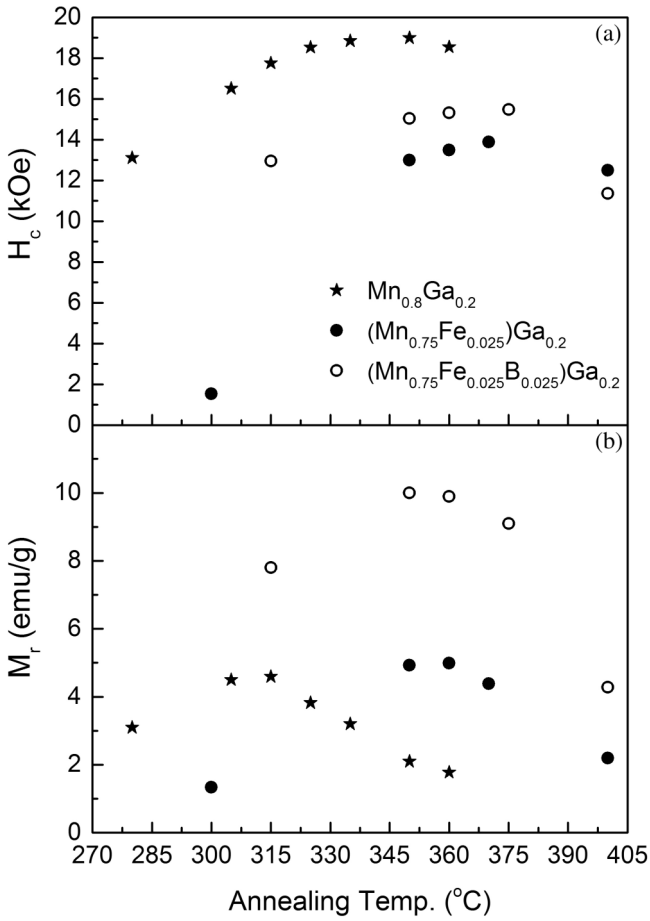

FIG. 4. (a) Coercivity, H_c, (b) remanence, M_r, of heat treated samples containing 5 at. % of a third element in place of Mn.

CONCLUSIONS

We have made a series of $(Mn_{0.8-x}X_x)Ga_{0.2}$ and $Mn_{0.8}(Ga_{0.2-x}X_x)$ alloys by ball milling, pressing and annealing at a range of temperatures. Samples were found to have a major phase of $(Mn,Fe)_3Ga$ or Mn_3 (Ga,Bi) similar to the Mn_3Ga with the tetragonal DO_{22} structure and exhibit significantly improved hard magnetic properties compared to Mn-Ga alloys. Samples were found to have coercivity H_c of 15.3 kOe and remanence M_r of 9.9 emu/g for a sample with optimized Fe and B contents, increasing the remanence by 115%. Samples with optimized Bi content have coercivity H_c of 16.6 kOe and remanence M_r of 7.4 emu/g, increasing the remanence by 60 %. We have shown that elemental substitution is an effective approach to increasing the magnetic remanence while maintaining a high coercivity.

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