High performance Nd-Fe-B permanent magnets without critical elements

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Abstract

Scanning electron microscopy, and magnetization measurements reveal that as cast $(\text{Nd}_{1-x}\text{Ce}_x)_2\text{Fe}_{14}\text{B}$ alloys contain significant amounts of α -Fe that can be dramatically reduced by annealing the alloys at 1000 °C for 3 days. The room temperature intrinsic coercivity, H_{ci} , of $(\text{Nd}_{0.8}\text{Ce}_{0.2})_{2.2}\text{Fe}_{14}\text{B}$ melt spun ribbons was found to be 11 kOe, which is ~32 to ~10% higher in comparison to that of $\text{Nd}_2\text{Fe}_{14}\text{B}$ ($H_{ci} = 8.3$ kOe), and $(\text{Nd}_{0.8}\text{Ce}_{0.2})_{2.0}\text{Fe}_{14}\text{B}$ ($H_{ci} = 10$ kOe), respectively. The substitution of Co for Fe in $(\text{Nd}_{0.8}\text{Ce}_{0.2})_2\text{Fe}_{14-z}\text{Co}_z\text{B}$ significantly increases both T_C and the maximum energy product, $(BH)_{max}$. Our study shows that both Co-containing and Co-free Ce-substituted $\text{Nd}_2\text{Fe}_{14}\text{B}$ alloys have excellent magnetic properties at room temperature and above. The experimental results also demonstrate the potential of Nd-Ce-Fe-TM-B based alloys as alternative to expensive Dy-containing high performance rare earth magnets.

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Introduction:

A broad class of existing permanent magnet (PM) materials can be divided into two large groups: i) rare-earth (RE) based PMs such as RE-Fe-B and Sm-Co, and ii) non-RE PMs such as Alnico, ferrites, Fe-Ni, and Mn-Bi. Magnets from the second group are generally unsuitable for electric motor applications in vehicles or wind turbines due to insufficient coercivity (Alnico) and/or low magnetization (ferrites) [1]. Therefore, discovery of low cost RE-based PMs or enhancing the performance of RE-free PMs that have large coercivity, H_{ci} , and remanence magnetization, B_r , is vitally important. Materials of choice for electric motors are presently based on a variety of Nd-Dy-Fe-B chemistries. Unfortunately, both Nd and Dy are considered critical elements based on supply risk versus importance to clean energy, [2] thus calling for suitable alternatives to replace Dy and overall reduction of Nd content in high-performance $Nd_2Fe_{14}B$ -based PMs.

Considering natural abundance and cost, La and Ce are possible low-cost alternatives to substitute for Nd in $Nd_2Fe_{14}B$. La is non-magnetic, and hence the substitution of La for Nd in Nd-Fe-B does not improve the properties required for a strong permanent magnet. However, in some cases La acts as a grain refiner [3]. Ce is another possible candidate where Ce valence may fluctuate between the moment-carrying Ce^{+3} (for $4f^1$ configuration) to the non-magnetic Ce^{+4} (for $4f^0$ electronic configuration) [4] resulting in a mixed valence state of 3.44 in $Ce_2Fe_{14}B$ [5]. To date, various studies on the development of low-cost Ce-doped RE-Fe-B magnets have been reported [6,7,8,9,10,11]. However, substitution of Ce for Nd in $Nd_2Fe_{14}B$ alloy deteriorates the hard magnetic properties due to the low Curie temperature, $T_c = 422$ K, low saturation magnetization

($4\pi M = 11.7$ kG), and low magnetocrystalline anisotropy fields H_a (30 kOe) of the pure $\text{Ce}_2\text{Fe}_{14}\text{B}$ phase [12].

Recently, we reported that by controlling the microstructure of $\text{Nd}_2\text{Fe}_{14}\text{B}$ with simultaneous substitution of Nd by Ce, and Fe by Co it is possible to develop low cost $(\text{Nd}_{0.8}\text{Ce}_{0.2})_{2.4}\text{Fe}_{12}\text{Co}_2\text{B}$ melt spun ribbons that have H_{ci} and $(BH)_{\max}$ values of 17.7 kOe, and 12.6 MGOe, respectively [13]. We also observed that critical concentration of Co in $(\text{Nd}_{1-x}\text{Ce}_x)_2\text{Fe}_{14-y}\text{Co}_y\text{B}$ depends on the amount of Ce present in the alloy [14]. For example, substitution of one or two Co atoms per formula unit for Fe provides optimum values of H_{ci} and $(BH)_{\max}$ in $(\text{Nd}_{0.8}\text{Ce}_{0.2})_2\text{Fe}_{14-y}\text{Co}_y\text{B}$ ($y = 1$) and $(\text{Nd}_{0.5}\text{Ce}_{0.5})_2\text{Fe}_{14-y}\text{Co}_y\text{B}$ ($y = 2$), respectively. Beyond these Co concentrations, the second quadrant of demagnetization curve becomes ill-defined and results in a low $(BH)_{\max}$. The effect of Co on hard magnetic properties for other concentrations of Ce in $(\text{Nd}_{1-x}\text{Ce}_x)_2\text{Fe}_{14-y}\text{Co}_y\text{B}$ remains to be determined. Here, we report the magnetic properties of both bulk polycrystalline, and rapidly solidified nanostructured ribbons of Ce and Co co-doped $(\text{Nd}_{1-x}\text{Ce}_x)_2\text{Fe}_{14-y}\text{Co}_y\text{B}$ ($0.2 \leq x \leq 1$, and $0 \leq y \leq 4$) compounds. We also studied effect of substitution of Fe by other transition metals such as Cr, V, Mn, Ni on hard magnetic properties of the Nd-Fe-B-based alloys.

Experimental methods:

The alloys (approximately 15 g each) were prepared by arc melting followed by drop casting through a ~ 9.6 mm diameter orifice at the following compositions:

and

The constituent elements, including lanthanides, were of high purity (99.9+ wt.%) and were obtained from the Materials Preparation Center at the Ames Laboratory. The melt-spun ribbons were prepared by induction melting the drop-cast ingots in a quartz crucible under 1/3 atm of high purity He gas and then ejected at 125 torr overpressure onto a copper chill wheel rotating at a tangential speed of ~25 m/s. The as-spun ribbons were annealed in helium atmosphere at different temperatures. The optimum temperature and time were found to be 600 °C, and 20 minutes, respectively. The magnetization measurements were performed in a Physical Property Measurement System (PPMS) made by Quantum Design Inc. in magnetic field up to 50 kOe and temperatures up to 1000 K. Microstructure, and energy-dispersive x-ray spectroscopy was carried out on a JEOL5910LV scanning electron microscope. The x-ray powder diffraction (XRD) parameters were obtained on a Rigaku TTRAX rotating anode powder diffractometer employing Mo- $K\alpha$ radiation. The phase and lattice parameters were determined from Rietveld analysis using LHPM Rietica [15].

Results and discussion:

The x-ray diffraction study of as-cast $(\text{Nd}_{1-x}\text{Ce}_x)_2\text{Fe}_{14}\text{B}$ showed four different phases: i) major phase 2:14:1; ii) the second most abundant phase α -Fe; iii) CeFe_2 for $x \geq 0.25$; and

iv) 2:17 phase for $x < 0.25$. The concentration of the 2:14:1 phase decreases, and the amount of other phases increase with Ce concentration (Table 1). The presence of a significant amount of Fe dendrites in the as-cast samples was also observed in the scanning electron micrographs (SEM) for the $(\text{Nd}_{0.8}\text{Ce}_{0.2})_2\text{Fe}_{14}\text{B}$ and $(\text{Nd}_{0.8}\text{Ce}_{0.2})_{2.2}\text{Fe}_{14}\text{B}$ samples (Fig. 1). The energy dispersive spectroscopy analysis shows that the gray/white areas are mainly the 2:14:1 phase, and the black areas are α -Fe dendrites (data are not shown). The SEM results along with the magnetization measurements showed that the amount of α -Fe decreases with increasing RE concentration beyond 2 atoms per formula unit (not shown). In order to complete solid state reactions and eliminate impurity phases, all bulk samples were heat treated at different temperatures. We found that drop-cast alloys annealed at 1000 °C for 3 days contain more than 97% of the main $\text{RE}_2\text{Fe}_{14}\text{B}$ phase with less than 2% of α -Fe impurity (Table 1), and no 2:17, or CeFe_2 phases.

The magnetization data as a function of magnetic field for melt spun ribbons at $T = 300\text{K}$ of $(\text{Nd}_{0.8}\text{Ce}_{0.2})_{2.2}\text{Fe}_{14}\text{B}$ (Fig. 2) show that adding a small over stoichiometric amount of rare earth significantly increases both the H_{ci} and $(BH)_{max}$. The respective values of H_{ci} and $(BH)_{max}$ are 11 kOe and 14.3 MGOe, respectively. These values are higher by ~32 to ~10% for H_{ci} and ~4 to ~30% for $(BH)_{max}$ when compared to those for $\text{Nd}_2\text{Fe}_{14}\text{B}$ ($H_{ci} = 8.3\text{ kOe}$, $(BH)_{max} = 13.8\text{ MGOe}$), and $(\text{Nd}_{0.8}\text{Ce}_{0.2})_{2.0}\text{Fe}_{14}\text{B}$ ($H_{ci} = 10\text{ kOe}$, $(BH)_{max} = 11\text{ MGOe}$), respectively. Figures 2a and 2b show $B(H)$ loops of $(\text{Nd}_{0.8}\text{Ce}_{0.2})_{2.2}\text{Fe}_{14}\text{B}$ measured at 300 K and 500 K, respectively. Both loops exhibit “knees” in the 3rd quadrant; this is important for electric motor applications. The H_{ci} and $(BH)_{max}$ for $(\text{Nd}_{0.8}\text{Ce}_{0.2})_{2.2}\text{Fe}_{14}\text{B}$ vary from 11 kOe and 14.3 MGOe at 300 K to 3.9 kOe

and 3.2 MGOe at 500 K, respectively (Figs. 2c-d). Considering our previous work [13] on optimization of magnetic properties by adding cobalt and ZrC, we have prepared $(\text{Nd}_{0.8}\text{Ce}_{0.2})_{2.2}\text{Fe}_{12}\text{Co}_2\text{B}+2.5\%$ ZrC melt spun ribbons. The H_{ci} , and $(BH)_{\text{max}}$ as a function of magnetic field are shown in Figs. 2c and 2d, respectively. Interestingly, the sample with no cobalt and no ZrC sample has a higher H_{ci} but a lower $(BH)_{\text{max}}$ from 300 to 500 K. The slightly better H_{ci} may be attributed to segregation of excess amount of rare earth into the grain boundaries as reported earlier [13]. We have heat treated the melt-spun ribbons at different temperatures and times and found that the heat treatment of the ribbons at 600 °C for 20 minutes have the optimized magnetic properties for both Ce and (Ce, Co) co-doped Nd-Fe-B samples (Fig. 3). We believe that the ribbons heat treated at 600 °C for 20 minutes and bulk samples heat treated at 1000 °C for 3 days have the optimized microstructure.

We have prepared several $(\text{Nd}_{1-x}\text{Ce}_x)_2\text{Fe}_{14-z}\text{Co}_z\text{B}$ ($0 \leq x \leq 0.75$), and $0 \leq z \leq 4$) alloys by arc melting followed by drop-casting, and heat treatment at 1000 °C, 3 days. All Co-substituted samples exhibited tetragonal $\text{RE}_2\text{Fe}_{14}\text{B}$ phase. The lattice parameters decrease with increasing Co concentration (data not shown), which can be attributed to the smaller radius ($CN = 12$) of Co (1.252 Å) compared to Fe (1.274 Å). The magnetization measurements show that Curie temperatures increase almost linearly with Co for all concentrations of Ce in $(\text{Nd}_{1-x}\text{Ce}_x)_2\text{Fe}_{14-z}\text{Co}_z\text{B}$ ($0 \leq x \leq 0.75$), and $0 \leq z \leq 4$) (Table 2).

The room temperature magnetization measurements of melt spun ribbons show lower values of (BH)max for the samples with $x = 0.25, 0.3$ and $z = 0$ in $(\text{Nd}_{1-x}\text{Ce}_x)_2\text{Fe}_{14-z}\text{Co}_z\text{B}$ (Fig. 4). These low values are due to the decrease in squareness of hysteresis loop which may be attributed to intergranular magnetically soft phases with Ce substitution [16]. The Curie temperature, T_C , is also decreasing with a Ce concentration. Substitution of Co for Fe increases T_C . The Co doped samples exhibit not only improved T_C but they also display enhanced permanent magnetic properties, and thus are promising for various applications. As shown in Fig. 4, Co additions dramatically change the undesirable BH loop behavior to a nearly perfect square magnetic hysteresis loop, while enhancing the (BH)max. For $x = 0.25$, (BH)max increases from 8.7 MGOe ($z = 0$) to 13 MGOe ($z = 1$ and 2). For $x = 0.30$, the (BH)max changes from 5.7 MGOe ($z = 0$) to 14.4 MGOe ($z = 1$). The change is more obvious in the demagnetization curves for $x = 0.3$ (see Fig. 4b).

We also investigated the permanent magnetic properties of the melt spun ribbons of several other $(\text{Nd}_{1-x}\text{Ce}_x)_{2+y}\text{Fe}_{14-z}\text{Co}_z\text{B}$ alloys for $x \leq 0.5$ and $y = 0$. The obtained values of (BH)max, Br, Hci, and T_C are summarized in Table 2. The yellow (online, or grey in print) highlighted (listed as bold *italic* values) rows in Table 2 represent the concentrations with (BH)max > 11 MGOe. As shown in Table 2, for all Ce concentrations (x), Co doping enhances (BH)max and Br. However, Co doping also results in a slight decrease of Hci. In all cases, Co doping enhances the T_C significantly. Based on the observations presented in Table 2, the $(\text{Nd}_{0.8}\text{Ce}_{0.2})_2\text{Fe}_{14-z}\text{Co}_z\text{B}$ ($z = 2$) alloy appears to be the composition with the most enhanced permanent magnetic properties including a high Curie temperature of 695 K.

The enhanced (BH)_{max} for certain critical concentrations of Ce and Co is due to a synergistic effect between Ce and Co in which the Co atom occupies Fe(4c) [17] site, while larger Ce³⁺ and smaller Ce⁴⁺ prefer RE(4g) and RE(4f) sites, respectively [18]. Here, the Fe(4c) sites are next to the RE(4g) and RE(4f) sites and the Co preferentially fills these Fe(4c) sites due to its strong affinity for the RE elements. The high coordination of Co surrounding the Ce shifts its valence more toward magnetic Ce³⁺. Therefore the improved magnetic properties can be attributed to the shift from the non-magnetic Ce⁴⁺ to the magnetic Ce³⁺.

An almost linear increase of T_C with increasing Co can be attributed to stronger exchange interactions between Co-Co, or Co-Fe compared to Fe-Fe [19]. The reduction of H_{ci}, and (BH)_{max} beyond the critical concentration of Co in (Nd_{0.8}Ce_{0.2})₂Fe_{14-z}Co_zB may be due to the additional Co atoms occupying other Fe sites as suggested by Mössbauer, neutron, and NMR [20,21,22,23] studies of Nd₂Fe_{14-z}Co_zB.

We have also studied the effect of substituting Co with other transition metals. A series of compounds was prepared with various combinations of other transition metals such as V, Cr, Mn, and Ni in the (Nd_{0.8}Ce_{0.2})₂Fe_{14-z}(Co, TM)_zB + 2.5% ZrC alloy where TM = V, Cr, Mn, and Ni. Here, we have presented only the relative concentration of (Co_{1.9}TM_{0.1}). Even though we do not have experimental evidence proving that TMs substitute for Co our previous experience with similar compounds (Ref. 14) indicates this as a lively scenario. Magnetization M(T) measurements show that T_C decreases with the addition

TM. For example, substitutions of Mn, or Cr for Co decrease T_C by about 40 K from 695 to ~650 K. Their room temperature magnetic properties: H_{ci} , $(BH)_{max}$ M_s and H_a were also measured. The room temperature magnetic hysteresis loops for the melt-spun ribbons of $(Nd_{0.8}Ce_{0.2})_2Fe_{12}(Co_{1.9}TM_{0.1})B+2.5\% ZrC$, $TM = V, Cr, Mn$, and Ni are shown in Fig. 5, where the intrinsic coercivity (H_{ci}) varies from 8.7 for Cr to 10.2 kOe, for V doped sample, which compares to $H_{ci} = 10.2$ kOe for the un-doped sample. Although, the substitution of Cr and Mn slightly decreases H_{ci} , the maximum energy product $((BH)_{max})$ increases (16.6 MGOe for Mn to 18.7 MGOe for Cr doped) compared to the earlier reported value for the unsubstituted of $(Nd_{0.8}Ce_{0.2})_2Fe_{12}Co_2B+2.5\% ZrC$ alloy $((BH)_{max} = 16.2$ MGOe, see Table 3). The composition of the Cr containing sample was further modified to $(Nd_{0.8}Ce_{0.2})_{2.4}Fe_{12}(Co_{1.9}Cr_{0.1})B + 2.5\% ZrC$, by adding an extra amount of Nd+Ce. At 300 K, H_{ci} increased to 16.8 kOe but $(BH)_{max}$ decreased to 9.8 kOe (Table 3). The saturation magnetization varies from 14.9 to 16.9 kG for $TM = V$, and Cr, respectively in $(Nd_{0.8}Ce_{0.2})_2Fe_{12}(Co_{1.9}TM_{0.1})B+2.5\% ZrC$ alloys. Similarly, the anisotropy field varies from 65 to 68.3 kOe for the respective alloys (Table 3).

We have further optimized the alloy composition by adding ZrC, and excess Nd and/or Ce in $(Nd_{1-x}Ce_x)_2Fe_{14-z}Co_zB$. It was shown that the addition of TiC or ZrC enhances glass-forming ability [24], reduces grain size, and produces a uniform microstructure [25,26]. The results for $(Nd_{0.8+x}Ce_{0.2})_{2+y}Fe_{12}Co_2B+2.5\% ZrC$ are shown in Fig. 6. When excess Nd and/or Ce are added, the coercivity can be significantly enhanced while maintaining the large $(BH)_{max}$, M_s and T_C values. Fig. 6a shows that addition of excess

(Nd+Ce) increases H_{ci} , and it tends to saturate for $x = 0.16$, and $y \geq 0.2$ in $(Nd_{0.8+x}Ce_{0.2})_{2+y}Fe_{12}Co_2B+2.5\% \text{ ZrC}$. The temperature dependence of H_{ci} for $x = 0.16$, $y = 0.4$ varies from ~ 18.9 kOe at 300 K to ~ 5.8 kOe at 500 K. Similarly, $(BH)_{max}$ varies from 15 MGOe at 300 K to 6.8 MGOe at 500 K for $x = 0.16$, $y = 0.4$. In addition, the high temperature (>450 K) H_{ci} and $(BH)_{max}$ values for $x = 0.16$, $y=0.2$, and 0.4 are higher than those of $x = 0.16$, $y = 0$. The temperature coefficient of the coercivity (β), and the temperature coefficient of Br (α) are $\sim -0.3 \text{ \% K}^{-1}$ to $-0.1 \text{ \% K}^{-1}$, respectively. The room temperature anisotropy, H_a , and remanence magnetization varies from 62 kOe, 8.4 kG for $x = 0$, $y = 0.4$ to 71.8 kOe, 8.6 kG for $(Nd_{0.8+x}Ce_{0.2})_{2+y}Fe_{12}Co_2B+2.5\% \text{ ZrC}$, $x = 0.16$, $y = 0.4$, respectively.

Conclusion:

In summary, we have investigated the hard magnetic properties of as cast and heat treated co-doped with Ce and Co $(Nd_{1-x}Ce_x)_2Fe_{14-z}Co_zB$ alloys in bulk polycrystalline and nanocrystalline melt-spun ribbon states. Experimentally we determine the various compositions of isotropic magnets with $T_C > 375 \text{ }^\circ\text{C}$ which have 300 K magnetic properties with $M_s > 13$ kG, H_{ci} between 10 and 19 kOe and $(BH)_{max}$ between 10 and 18 MGOe. The values of the temperature coefficient of the Br (α), and coercivity (β) are $-0.1\% / ^\circ\text{C}$ and $-0.3 \text{ \% } / ^\circ\text{C}$, respectively. These magnetic properties are superior to those of several recently reported Ce-substituted Nd-Fe-B based alloys [27,28]. We also observed that in addition to Co, Mn and Cr can be substituted for Fe while retaining good magnetic properties in $(Nd_{0.8}Ce_{0.2})_2Fe_{12}(Co_{1.9}TM_{0.1})B+2.5\% \text{ ZrC}$, $TM = V, Cr, Mn$, and Ni. Although Co was once (in 1980's-1990's) considered to be a critical element, today

there are several sources in few countries located in various parts of the world, so the supply of Co is not critical, but the metal is still relatively expensive. Our study alleviates the criticality of Dy and Nd by substitution of Ce which is the most abundant and lowest cost rare earth element. The cost of components in the Ce, Co co-doped alloys is significantly lower compared to the $\text{Nd}_2\text{Fe}_{14}\text{B} + 2\% \text{ Dy}$ alloy which makes the materials described here attractive alternatives for Dy containing Nd-Fe-B magnets.

Acknowledgements

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Figure and Table Captions:

Fig. 1: Backscattered electron SEM images of the as cast $(\text{Nd}_{0.8}\text{Ce}_{0.2})_{2.0}\text{Fe}_{14}\text{B}$ (left), and $(\text{Nd}_{0.8}\text{Ce}_{0.2})_{2.2}\text{Fe}_{14}\text{B}$ (right) samples. The gray/white area is the 2:14:1 phase, and dark black area is the Fe dendrites.

Fig. 2 (color online): Magnetization as function of magnetic field for melt spun ribbons (a) $(\text{Nd}_{0.8}\text{Ce}_{0.2})_{2.2}\text{Fe}_{14}\text{B}$ at 300 K and (b) 500 K (b). $B (H+4\pi M)$ vs H curves show “knees” (dotted circle) in the 3rd quadrant up to 500 K (227 °C). (c) Intrinsic coercivity, H_{ci} vs. temperature and (d) maximum energy product, $(BH)_{\text{max}}$, vs. temperature for melt spun ribbons $(\text{Nd}_{0.8}\text{Ce}_{0.2})_{2.2}\text{Fe}_{14}\text{B}$ and $(\text{Nd}_{0.8}\text{Ce}_{0.2})_{2.2}\text{Fe}_{12}\text{Co}_2\text{B}+2.5\% \text{ ZrC}$.

Fig. 3 (color online): Magnetization as function of magnetic field for melt spun ribbons (a) $(\text{Nd}_{0.75}\text{Ce}_{0.25})_2\text{Fe}_{14}\text{B}$, and (b) $(\text{Nd}_{0.8}\text{Ce}_{0.2})_2\text{Fe}_{12}\text{Co}_2\text{B}$ heat treated at different temperatures.

Fig. 4 (color online): Magnetization versus magnetic field for melt spun ribbons (a) $(\text{Nd}_{0.75}\text{Ce}_{0.25})_2\text{Fe}_{14-z}\text{Co}_z\text{B}$ and (b) $(\text{Nd}_{0.7}\text{Ce}_{0.3})_2\text{Fe}_{14-z}\text{Co}_z\text{B}$.

Fig. 5 (color online): Room temperature magnetization versus magnetic field for melt spun ribbons $(\text{Nd}_{0.8}\text{Ce}_{0.2})_2\text{Fe}_{12}(\text{Co}_{1.9}\text{TM}_{0.1})\text{B}+2.5\% \text{ ZrC}$, TM = (a) V, (b) Cr, (c) Mn, and (d) Ni.

Fig. 6 (color online): (a) Intrinsic coercivity, H_{ci} vs. temperature, and (b) maximum energy product, $(BH)_{max}$ vs. temperature for melt spun ribbons $(Nd_{0.8+x}Ce_{0.2})_{2+y}Fe_{12}Co_2B+2.5\% ZrC$.

Table Captions:

Table 1: Phase contents of drop cast $(Nd_{1-x}Ce_x)_2Fe_{14}B$ alloys in as-cast (straight font) and heat treated (bold *italic*) state in wt.%.

Table 2 (color online): Room temperature values of maximum energy product $(BH)_{max}$, remanence magnetization (Br) , intrinsic coercivity H_{ci} , Curie temperature T_C of $(Nd_{1-x}Ce_x)_2Fe_{14-z}Co_zB$ melt spun ribbons heat treated for 20 minutes at 600 °C. The yellow highlighted (listed as bold *italic* values) rows represent the concentrations with $(BH)_{max} > 11$ MGOe.

Table 3: The room temperature magnetic properties: coercivity (H_{ci}), maximum energy product $((BH)_{max})$, saturation magnetization (M_s), and anisotropy field (H_a) of $(Nd_{0.8}Ce_{0.2})_2Fe_{12}(Co_{1.9}TM_{0.1})B + 2.5\% ZrC$, $TM = V, Cr, Mn, \text{ and } Ni$. For comparison, the corresponding values of the unsubstituted $(Nd_{0.8}Ce_{0.2})_2Fe_{12}Co_2B+2.5\% ZrC$ sample are also provided in the bottom row.

Fig. 1: Backscattered electron SEM images of the as cast $(\text{Nd}_{0.8}\text{Ce}_{0.2})_{2.0}\text{Fe}_{14}\text{B}$ (left), and $(\text{Nd}_{0.8}\text{Ce}_{0.2})_{2.2}\text{Fe}_{14}\text{B}$ (right) samples. The gray/white area is the 2:14:1 phase, and dark black area is the Fe dendrites.

Fig. 2 (color online): Magnetization as function of magnetic field for melt spun ribbons (a) $(\text{Nd}_{0.8}\text{Ce}_{0.2})_{2.2}\text{Fe}_{14}\text{B}$ at 300 K and (b) 500 K. B ($H + 4\pi M$) vs H curves show “knees” (dotted circle) in the 3rd quadrant up to 500 K (227°C). (c) Intrinsic coercivity, H_{ci} vs. temperature and (d) maximum energy product, $(BH)_{max}$, vs. temperature for melt spun ribbons $(\text{Nd}_{0.8}\text{Ce}_{0.2})_{2.2}\text{Fe}_{14}\text{B}$ and $(\text{Nd}_{0.8}\text{Ce}_{0.2})_{2.2}\text{Fe}_{12}\text{Co}_2\text{B} + 2.5\%\text{ ZrC}$.

Fig. 3 (color online): Magnetization as function of magnetic field for melt spun ribbons

(a) $(\text{Nd}_{0.75}\text{Ce}_{0.25})_2\text{Fe}_{14}\text{B}$, and (b) $(\text{Nd}_{0.8}\text{Ce}_{0.2})_2\text{Fe}_{12}\text{Co}_2\text{B}$ heat treated at different

temperatures.

Fig. 3

Fig. 4 (color online): Magnetization versus magnetic field for melt spun ribbons (a)

$(\text{Nd}_{0.75}\text{Ce}_{0.25})_2\text{Fe}_{14-z}\text{Co}_z\text{B}$ and (b) $(\text{Nd}_{0.7}\text{Ce}_{0.3})_2\text{Fe}_{14-z}\text{Co}_z\text{B}$.

Fig. 5

Fig. 5 (color online): Room temperature magnetization versus magnetic field for melt spun ribbons $(Nd_{0.8}Ce_{0.2})_2Fe_{12}(Co_{1.9}TM_{0.1})B+2.5\%$ ZrC, TM = (a) V, (b) Cr, (c) Mn, and (d) Ni.

Fig. 6

Fig. 6 (color online): (a) Intrinsic coercivity, H_{ci} vs. temperature, and (b) maximum energy product, $(BH)_{\text{max}}$ vs. temperature for melt spun ribbons

$(\text{Nd}_{0.8+x}\text{Ce}_{0.2})_{2+y}\text{Fe}_{12}\text{Co}_2\text{B} + 2.5\% \text{ZrC}$.

Table 1: Phase contents of drop cast (Nd_{1-x}Ce_x)₂Fe₁₄B alloys in as-cast (straight font) and heat treated (bold *italic*) state in wt.%.

Ce x	RE ₂ Fe ₁₄ B (%)	RE ₂ Fe ₁₇ %	α -Fe %	CeFe ₂ %
0	81.77 98.59	3.66 0	14.57 1.41	0 0
0.05	80.06 98.44	3.66 0	16.28 1.56	0 0
0.1	73.65 99.05	5.88 0	20.47 0.95	0 0
0.15	78.31 99.19	3.98 0	17.71 0.81	0 0
0.2	83.05 99.54	3.3 0	13.65 0.46	0 0
0.25	82.93 99.06	0 0	14.99 0.94	2.08 0
0.50	73.43 98.92	0 0	17.50 1.59	9.07 0
0.75	65.51 98.92	0 0	19.31 1.08	15.18 0
1	46.88 98.49	0 0	32.32 1.51	20.80 0

Table 2 (color online): Room temperature values of maximum energy product (BH)_{max}, remanence magnetization (Br), intrinsic coercivity H_{ci}, Curie temperature T_C of (Nd_{1-x}Ce_x)₂Fe_{14-z}Co_zB melt spun ribbons heat treated for 20 minutes at 600 °C. The yellow highlighted (listed as bold *italic* values) rows represent the concentrations with (BH)_{max} > 11 MGOe.

(Nd_{0.8}Ce_{0.2})₂Fe_{14-z}Co_zB, x = 0.2

z	(BH) _{max} (MGOe)	Br (kG)	H _{ci} (kOe)	T _C (K)
0	10.6	8.6	10	546
1	11.2	8.6	6.4	620
1.5	10.5	9	5.6	662
1.75	13.2	8.9	7.5	670
2	16	9	7.8	695
2.25	14.3	9.2	6.8	707
2.5	13.5	8.9	6.2	720

(Nd_{0.75}Ce_{0.25})₂Fe_{14-z}Co_zB, x=0.25

0	8.4	8.1	9	540
1	13	9.5	5.5	615
2	13	8.9	6.9	682

(Nd_{0.7}Ce_{0.3})₂Fe_{14-z}Co_zB, x=0.3

0	5.7	7.3	7.8	540
1	14.4	9.2	6.8	608
2	11.5	8.6	6.5	670

(Nd_{0.65}Ce_{0.35})₂Fe_{14-z}Co_zB, x=0.35

0	10.7	8.8	6	535
1	12	8.6	6	--
2	12.2	8.7	6.4	670

(Nd_{0.5}Ce_{0.5})₂Fe_{14-z}Co_zB, x=0.5

0	9.5	7.9	4.9	520
0.5	10.1	9.06	4.3	548
1	14.6	8.2	8	590
1.5	12	8.6	5.5	608
2	7.6	7.8	4.8	636
4	8.02	8.3	4.4	750

Table 3: The room temperature magnetic properties: coercivity (H_{ci}), maximum energy product ($(BH)_{max}$), saturation magnetization (M_s), and anisotropy field (H_a) of

$(Nd_{0.8}Ce_{0.2})_2Fe_{12}(Co_{1.9}TM_{0.1})B + 2.5\% \text{ ZrC}$, $TM = V, Cr, Mn$, and Ni . For comparison, the corresponding values of the unsubstituted $(Nd_{0.8}Ce_{0.2})_2Fe_{12}Co_2B + 2.5\% \text{ ZrC}$ sample are also provided in the bottom row.

Samples	H_{ci} kOe	$(BH)_{max}$ MGOe	M_s kG	H_a kOe
$(Nd_{0.8}Ce_{0.2})_2Fe_{12}Co_{1.9}V_{0.1}B + 2.5\% \text{ ZrC}$	10.2	11.3	14.9	65
$(Nd_{0.8}Ce_{0.2})_2Fe_{12}Co_{1.9}Cr_{0.1}B + 2.5\% \text{ ZrC}$	8.7	18.7	16.9	68.3
$(Nd_{0.8}Ce_{0.2})_2Fe_{12}Co_{1.9}Mn_{0.1}B + 2.5\% \text{ ZrC}$	8.9	16.6	16.1	67.2
$(Nd_{0.8}Ce_{0.2})_2Fe_{12}Co_{1.9}Ni_{0.1}B + 2.5\% \text{ ZrC}$	9.3	13	15.3	66.1
$(Nd_{0.8}Ce_{0.2})_2Fe_{12}Co_{1.9}Cr_{0.1}B + 2.5\% \text{ ZrC}$	16.8	9.8	12.7	66.2
$(Nd_{0.8}Ce_{0.2})_2Fe_{12}Co_2B + 2.5\% \text{ ZrC}$	10.2	16.2	16.4	68.3

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