Optimizing the magnetic properties of Ce-containing Nd–Fe–B sintered magnets with La substitution

Z Li, W Q Liu, Z P Zhang, D Wu, Y Q Li and M Yue
College of Materials Science and Engineering, Key Laboratory of Advanced Functional Materials, Ministry of Education of China, Beijing University of Technology, Beijing 100124, People’s Republic of China
E-mail: yueming@bjut.edu.cn

Keywords: Ce-containing Nd–Fe–B sintered magnets, CeFe2 phase, La substitution, magnetic properties, grain boundary

Abstract
Ce and La–Ce containing magnets with the compositions of [(La0.4Ce0.6)0.4Nd0.6]31.5FeBalM2.02B0.96 and (Ce0.4Nd0.6)31.5FeBalM2.02B0.96 were prepared by traditional sintering process. The results shows La substitution for Ce occurs in the 2:14:1 matrix phase which suppress the formation of the nonmagnetic CeFe2 phase in the magnet. Moreover, compared to the Ce containing magnet, the grain boundary (GB) phase is thinner and very continuous in the La–Ce containing magnet. The coercivity and the maximum energy product of La–Ce containing magnet increased by 2 kOe and 1.5 MGOe, respectively.

1. Introduction
Rare-earth permanent magnets play a critical role in the development of electric motors, hybrid vehicles, wind generators, and electronic communication devices [1–8]. Specially, the rapid growth of Nd–Fe–B sintered permanent magnets consumes a large quantify of rare earth elements, such as Nd and Pr. Meanwhile, it causes the overstock of abundant rare earth elements, such as La and Ce, leading to the imbalance utilization of rare-earth resources. Therefore, researchers focus on reducing the cost of Nd–Fe–B magnets by Ce substitution and comprehensive utilization of rare earth resources.

Recently, various attempts have been made to prepare Ce-containing Nd–Fe–B sintered magnets [9–13]. However, the magnetic properties of the magnets deteriorated after Ce substitution due to the poor intrinsic properties of the CeFe2 phase, compared with the Nd2Fe14B phase [14]. Moreover, Herbst et al found that the magnetic properties of CeFe2 phase deteriorated due to the existence of the CeFe2 phase, which decreased the ratio of the 2:14:1 phase in the magnets [15]. It is generally accepted that the CeFe2 phase forms easily in Nd–Fe–B magnets with high Ce content, undermining the magnetic properties of these magnets [16, 17]. In order to eliminate the CeFe2 phase, La can be introduced into the Ce–Fe–B ribbons and sintered magnets. In a previous study, we found that La substitution for Ce inhibits the formation of the CeFe2 phase in melt-spun (La/Ce)2Fe14B ribbons [18]. Liu et al also verified that La substitution for Ce could effectively inhibit the precipitation of the CeFe2 phase in melt-spun (La/Ce)2Fe14B ribbons [19]. Shi et al [20] prepared Ce–Fe–B and (La13Ce03)–Fe–B strips, and they found that the CeFe2 phase was drastically decreased from 67.1% to 38.1% by La substitution for 35% Ce. However, the CeFe2 phase were not diminished in the sintered magnet.

Most previous studies of La substitution for Ce to inhibit the formation of the CeFe2 phase have focused on melt-spun ribbons, but very little is known for sintered magnets. Compared to melt-spun ribbons, sintered magnets are more worthy of investigating due to their widespread application. In this work, Ce-containing and (LaCe)-containing Nd–Fe–B sintered magnets with nominal compositions of (Ce0.4Nd0.6)31.5FeBalM2.02B0.96 and (La0.16Ce0.24Nd0.6)31.5FeBalM2.02B0.96 were prepared. Subsequently, the properties and structures of the two sintered magnets were investigated to provide a technical guide for the preparation of La and/or Ce containing Nd–Fe–B sintered magnets with high magnetic properties.
2. Experimental

\((\text{Ce}_{0.4}\text{Nd}_{0.6})_{31.5}\text{Fe}_{81.5}\text{M}_{2.0}\text{B}_{0.96}\) (Magnet A) (M = Al, Cu, Ga, Zr, in wt\%) and
\([(\text{La}_{0.4}\text{Ce}_{0.6})_{31.5}\text{Fe}_{81.5}\text{M}_{2.0}\text{B}_{0.96}\) (Magnet B) were prepared. Each component was subjected to induction melting, hydrogen decrepitation, and jet milling. The final powders with a mean particle size of 3–5 \(\mu\)m were pressed and aligned under a compressive pressure of 5.5 MPa in a perpendicular magnetic field of 1.5 T followed by isostatic pressing of 225 MPa. The final magnets were prepared by sintering at 1333 K for 3 h, followed by a two-step annealing treatment at 1173 K for 2 h and 753 K for 3 h.

X-ray diffraction (XRD) with Cu K\(\alpha\) radiation was used to determine the crystal structure. The magnetic properties of the magnets were measured by a close-circuit permanent magnetic measurement system (NIM-500C). The microstructure of the magnets was observed by scanning electron microscope (SEM, Nova Nano200) with energy-dispersive x-ray spectroscopy and electron-probe microanalyzer (EPMA, JEOL JXA-800) with a wavelength-dispersive x-ray detector. Transmission electron microscopy (TEM) was performed using a JEM-2100F microscope.

3. Results and discussion

Figure 1 shows the demagnetization curves of magnets A and B. The derived magnetic properties of coercivity \(H_{cj}\), remanence \(B_r\) and energy product \((BH)_{max}\) are also given in the figure. The \(B_r\) of magnets A and B are 11.7 kG, but the \(H_{cj}\) of 5.3 kOe of magnet A is 2 kOe lower than that of magnet B. As a result, the \((BH)_{max}\) of magnet A is 1.5 MGOe lower than that of magnet B. Clearly the La partial substitution of Ce in the magnet was enhanced the overall magnetic properties. Nevertheless, it is necessary to determine the origin of the magnetic property enhancement in magnets A and B.

The phase compositions of the two magnets were analyzed by XRD with the Rietveld method, and the results are shown in figure 2. It can be seen in figure 2(a) that the sharpest diffraction peaks correspond to the tetragonal \((\text{Ce, Nd})_2\text{Fe}_{14}\text{B}\) matrix phase. However, the peaks at the 2\(\theta\) angles of 21.0°, 34.6° and 40.8° in the XRD pattern of magnet A correspond to the \((111), (022)\) and \((113)\) peaks of the cubic \(\text{CeFe}_2\) phase. With the La substitution, as shown in figure 2(b), the \(\text{CeFe}_2\) phase no longer exists in magnet B, indicating that the \(\text{CeFe}_2\) phase can be inhibited by La substitution [21].

The lattice parameters and mass fractions of the phases in magnet A and magnet B evaluated by the Rietveld XRD analysis are listed in table 1. The mass fraction of the \((\text{Ce, Nd})_2\text{Fe}_{14}\text{B}\) matrix phase, \(\text{CeFe}_2\) phase, and RE-rich phase in magnet A are 92.2 wt\%, 5.5 wt\% and 2.3 wt\%, respectively. With the La substitution, the mass fraction of \((\text{La–Ce, Nd})_2\text{Fe}_{14}\text{B}\) matrix phase and RE-rich phase increases to 96.3 wt\% and 3.7 wt\%, respectively. More importantly, the mass fraction of \(\text{CeFe}_2\) phase decreases to 0 by La substitution in magnet B.

The lattice parameters of the \((\text{Ce, Nd})_2\text{Fe}_{14}\text{B}\) matrix phase in magnet A are \(a = 8.783(2)\) Å and \(c = 12.113(2)\). With La substitution, the lattice parameters of the \((\text{La–Ce, Nd})_2\text{Fe}_{14}\text{B}\) matrix phase increase to \(a = 8.787(1)\) Å and \(c = 12.191(2)\) Å, indicating that La partially substitutes Ce in the 2:14:1 matrix phase because La has a
larger atomic radius than Ce. Moreover, the change of the lattice parameters of the RE-rich phase is larger compared to the 2:14:1 matrix phase, indicating that the La is more likely to enter the RE-rich phase. The result is in agreement with the calculations of Liu [22]. On the other hand, the lattice parameter of the CeFe2 phase in magnet A is $a = 7.338(2)$ Å. There is no CeFe2 phase in magnet B, indicating that CeFe2 phase can be inhibited by La substitution.

Furthermore, the elemental contents of region 1 to 5 were tested by EDS point scanning, and the results are shown in table 2. As shown in figure 3(a), the gray areas, the light gray areas, and the white areas are identified as the 2:14:1 matrix phase, the CeFe2 phase, and the RE-rich phase, respectively. It can be seen that the CeFe2 phases are located at region 1 in magnet A, and the contents of Ce and Fe are consistent with the stoichiometry of the CeFe2 phase. Only the 2:14:1 matrix phase and the RE-rich phase exist in magnet B, as shown in figure 2(b).

To follow the effect of La substitution on the grain boundary (GB) microstructure, SEM and TEM characterizations were carried out, as shown in figure 4. Figures 4(a) and (d) shows the BSE images of magnet A and magnet B. It can be seen that the GB phase in magnet B exhibits more continuity compared to magnet A. As shown in figure 4(b), the 2:14:1 matrix phase in magnet A was identified by the SAED patterns in the illustration, taken along the [001] zone axes. TEM characterizations conducted from magnet B are also shown in figure 4(e). Figures 4(c) and (f) show the different HRTEM pictures of typical GB morphology of the two magnets. The GB phase in figure 4(c) looks poorly distinct. However, the GB phase in figure 4(f) is thinner and continuous (4.86 nm). La substitution could result in a coercivity enhancement to 7.3 kOe, which could explain the difference between the high-resolution TEM images, as shown in figures 4(f) and (c). This GB phase magnetically insulates the matrix phase grains and increases the resistance to demagnetization. Even in cases where the layer is extremely thin, the coercivity could be enhanced if the interface is smooth enough, and no soft magnetic phases exist within the GB phase [23].
| Magnet | 2:14:1 matrix phase (P4_2/mmm) | CeFe₂ phase (Fd₃m) | RE-rich phase (P₆₃/mmc) |
|--------|---------------------------------|--------------------|------------------------|
|        | Mass fraction (wt%) | Lattice parameters (Å) | Mass fraction (wt%) | Lattice parameters (Å) | Mass fraction (wt%) | Lattice parameters (Å) |
| A      | 92.2                          | a = 8.783(2); c = 12.183(1) | 5.5                  | a = 7.338(2)          | 2.3                  | a = 3.876(1); c = 7.063(4) |
| B      | 96.3                          | a = 8.787(1); c = 12.191(2) | —                    | —                    | 3.7                  | a = 4.015(2); c = 7.235(3) |
4. Conclusion

Ce-containing and La–Ce-containing Nd–Fe–B magnets with compositions of \((\text{Ce}_{0.4}\text{Nd}_{0.6})_{31.5}\text{Fe}_{2.0}\text{Al}_{2.0}\text{B}_{0.96}\) and \(((\text{La}_{0.4}\text{Ce}_{0.6})_{0.4}\text{Nd}_{0.6})_{31.5}\text{Fe}_{2.0}\text{Al}_{2.0}\text{B}_{0.96}\) were prepared. Partial La substitution for Ce occurs in the 2:14:1

---

Table 2. The weight percentage of different phases in the two magnets.

| Region | Nd (at%) | Ce (at%) | Fe (at%) | La (at%) |
|--------|----------|----------|----------|----------|
| 1      | —        | 31.42    | 67.06    | —        |
| 2      | 8.58     | 5.91     | 85.51    | —        |
| 3      | 65.07    | 21.72    | 13.21    | —        |
| 4      | 63.24    | 0.97     | 12.81    | 14.22    |
| 5      | 8.61     | 3.54     | 85.47    | 2.38     |

---

Figure 3. The BSE and EPMA graphs of magnet A and B, (a) is magnet A and (b) is magnet B.

Figure 4. SEM and TEM characterizations for magnet A and B. (a) BSE images for magnet A, (b) Bright-field image and SAED pattern for magnet A (c) TEM images with a high magnification taken from region I in (b); (d) BSE images for magnet B, (e) Bright-field image and SAED pattern for magnet B (f) TEM images with a high magnification taken from region II in (e).
matrix phase which suppress the formation of the nonmagnetic CeFe₂ phase in the magnet. Moreover, compared to the Ce-containing magnet, the GB phase is thinner and very continuous in the LaCe-containing magnet. Therefore, better magnetic properties of $H_C$ of 7.3 kOe, $B_r$ of 11.7 kG and $(BH)_{\text{max}}$ of 32.1 MGOe were obtained in the LaCe-containing Nd–Fe–B sintered magnet.

Acknowledgments

This work was supported by the National Key Research and Development Program of China under Grant 2016YFB0700902; National Natural Science Foundation of China under Grant 51371002; International S&T Cooperation Program of China under Grant 2015DFG52020, Program of Top Disciplines Construction in Beijing under Grant PX2019_014204_500031.

ORCID iDs

D Wu https://orcid.org/0000-0001-8231-1045
Y Qi Li https://orcid.org/0000-0001-6943-6839
M Yue https://orcid.org/0000-0002-3633-1229

References

[1] Sagawa M, Fujimura S, Togawa N, Yamamoto H and Matsuura Y 1984 New material for permanent magnets on a base of Nd and Fe (invited) J. Appl. Phys. 55 2083
[2] Li X H, Hou L, Song W P, Huang G W, Hou F C, Zhang Q, Zhang H T, Xiao J W, Wen B and Zhang X Y 2017 Novel bimorphological anisotropic bulk nano composite materials with high energy products Adv. Mater. 29 1608490
[3] Li X H, Hou L, Song W, Zhang Q, Huang G W, Hua Y X, Zhang H T, Xiao J W, Wen B and Zhang X Y 2017 Controllably manipulating three-dimensional hybrid nanostructures for bulk nanocomposites with large energy products Nano Lett. 17 2985–93
[4] Li H L, Li X H, Guo D F, Lou L, Li W and Zhang X Y 2016 Three-dimensional self-assembly of core/shell-like nanostructures for high-performance nanocomposite permanent magnets Nano Lett. 16 5631–8
[5] Li H L, Lou L, Hou F C, Guo D F, Li W, Li X H, Gunderov D V, Sato K and Zhang X Y 2013 Simultaneously increasing the magnetization and coercivity of bulk nanocomposite magnets via severe plastic deformation Appl. Phys. Lett. 103 142406
[6] Liu Y G, Xu L, Wang Q F, Li W and Zhang X Y 2009 Development of crystal texture in Nd–lean amorphous Nd₃Fe₁₇B₁₀, under hot deformation Appl. Phys. Lett. 94 172502
[7] Guttleisch O, Willard M A, Bruck E, Chen C H, Sankar S G and Liu J P 2011 Magnetic materials and devices for the 21st century: Stronger, lighter, and more energy efficient Adv. Mater. 23 821–42
[8] Tang W, Jin T Z, Zhang J R, Gu G, Li J M and Du Y W 1998 Effect of composition on crystalline texture and magnetic properties of Nd₇Fe₁₉B₁₀ thin films J. Magn. Magn. Mater. 185 241–5
[9] Zhang L L, Li Z B, Ma Q, Li Y F, Zhao Q and Zhang X F 2017 Coercivity enhancement in (Ce,Nd)–Fe–B sintered magnets prepared by adding NdH₃ powders J. Magn. Magn. Mater. 435 96–9
[10] Zhang L L, Li Z B, Zhang X F, Ma Q, Liu L Y, Li F and Zhao Q 2017 Uniform magnetization reversal in dual main-phase (Ce, Nd₃)Fe₁₉B₁₀ sintered magnets with in homogeneous microstructure J. Phy. D: Appl. Phys. 50 065001
[11] Huang S L, Feng H B, Zhu M G, Li H H, Li Y F, Sun Y C, Zhang Y and Li W 2013 Optimal design of sintered Ce₃Nd₂Fe₁₄B₁₀ magnets with a low-melting-point Ce₃Nd₃-rich phase Int. J. Miner. Metall. Mater. 22 117–22
[12] Li Z, Liu W, Zhu S S, Li Y Q, Wang Y Q, Zhang D T, Yue M, Zhang J X and Huang X L 2013 Effects of Ce substitution on the microstructures and intrinsic magnetic properties of Nd–Fe–B alloy J. Magn. Magn. Mater. 393 551–4
[13] Zhang Y J, Ma T Y, Yan M, Jin J Y, Wu B, Peng B X, Liu Y S, Yue M and Liu C Y 2018 Post-sinter annealing influences on coercivity of multi-main-phase Nd–Ce–Fe–B magnets Acta Mater. 146 97–105
[14] Herbst J F 1991 R₂Fe₁₄B materials: intrinsic properties and technological aspects Rev. Mod. Phys. 63 819–98
[15] Herbst J F, Meyer M S and Pinkerton F E 2012 Magnetic hardening of Ce₂Fe₁₄B J. Appl. Phys. 111 07A718
[16] Yan C J, Guo S, Chen R J, Lee D and Yan A R 2014 Effect of Ce on the magnetic properties and microstructure of sintered Didymium-Fe-B magnets IEEE Trans. Magn. 50 2102605
[17] Fan X D, Guo S, Chen K, Chen R J, Lee D and You C Y 2016 Tuning Cé distribution for high performance Nd–Fe–B sintered magnets J. Magn. Magn. Mater. 419 394–9
[18] Lu Q M, Niu J, Liu W Q, Yue M and Altounian Z 2017 Enhanced magnetic properties of spark plasma sintered (La/Ce)–Fe–B–B magnets IEEE Trans. Magn. 53 2100603
[19] Liao X F, Zhang J S, Yu H Y, Zhong X C, Zhao L Z, Xu K, Peng D R and Liu Z W 2019 Maximizing the hard magnetic properties of melt-spin Ce-La–Fe–B alloys J. Mater. Sci. 54 7288–99
[20] Shi Q, Liu Y, Li J, Zhao W, Wang B Q and Gao X 2019 Significant improvement of the 2:14:1 phase formability and magnetic properties of multi-phases RE–Fe–B magnets with La substitution for Ce J. Magn. Magn. Mater. 476 1–6
[21] Liu W, Zhang Z P, Yue M, Li Z, Zhang D T and Zhang H G 2018 Effects of La substitution on the crystal structure and magnetization of MMFe-B alloy (MM = La, Ce, Pr, Nd) J. Magn. Magn. Mater. 464 61–4
[22] Liu X B, Altounian Z, Huang M, Zhang Q and Liu J P 2013 The partitioning of La and Y in Nd–Fe–B magnets: a first-principles study J. Alloy. Compd. 549 366–9
[23] Viala F, Joly F, Nevalainen E, Sagawac M, Hiragad K T and Parkd K 2002 Improvement of coercivity of sintered NdFeB permanent magnets by heat treatment J. Magn. Magn. Mater. 245 1329–34