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Crystallographic and magnetic properties of the quaternary rare-earth–transition-metal boron nitrides $R_2Fe_{14}BN_{0.1}$ ($R = Nd$ and Sm)

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Received 24 November 1998, in final form 24 March 1999

Abstract. Quaternary rare-earth–transition-metal boron nitrides, $R_2Fe_{14}BN_{0.1}$ ($R = Nd$ and Sm), have been synthesized by arc melting. The bond of boron nitride (BN) can be broken by arc melting to allow combination with rare-earth and transition-metal atoms. The structure and magnetic properties of these quaternary compounds have been studied by means of x-ray diffraction, neutron diffraction, and alternating-current initial-susceptibility and magnetization measurements. The $R_2Fe_{14}BN_{0.1}$ ($R = Nd$ and Sm) compounds have the tetragonal $Nd_2Fe_{14}B$ -type structure with space group $P4_2/mnm$. The Curie temperature and magnetic anisotropy of the compound $Nd_2Fe_{14}B$ are slightly enhanced by introducing nitrogen into the lattice of $Nd_2Fe_{14}B$. The spin-reorientation temperature of $Nd_2Fe_{14}BN_{0.1}$ is the same as that of $Nd_2Fe_{14}B$.

1. Introduction

Since they were discovered in 1984 [1], the structure and magnetic properties of the ternary compounds of the type $R_2Fe_{14}B$ ($R =$ rare-earth elements) have been studied by numerous investigators [1–4]. Magnetic measurements showed that $R_2Fe_{14}B$ compounds have high Curie temperatures and some of them have a sufficiently high magnetization and magnetocrystalline anisotropy for application as permanent magnets. Only carbon has been reported capable of replacing boron in $R_2Fe_{14}B$ and forming carbides with the $Nd_2Fe_{14}B$ structure [5].

It has been found that rare-earth–iron intermetallics of the R_2Fe_{17} type and $RFe_{11}Ti$ type can absorb moderate quantities of nitrogen [6, 7]. The nitrides retain the structure of the virgin compounds, and introduction of nitrogen into the lattice leads to drastic changes of the magnetic properties. Zhang *et al* reported that the nitrides $R_2Fe_{14}BN_x$ ($R = Y, Nd$) can be prepared by gas reaction [8]. Until now, the main disadvantage of the nitrated rare-earth–iron intermetallics has been their low thermal stability—they are easily turned into RN_x and α -Fe phases at high temperatures.

In our recent work, by using mechanical alloying, we successfully broke the bond of boron nitride, BN, allowing combination with Nd and Fe to form $Nd_2Fe_{14}BN_x$ alloys with $H_c = 20$ kOe [9]. It is interesting to test whether the chemical bond of boron nitride can be broken by arc melting to allow combination with rare-earth elements and Fe to form $R_2Fe_{14}BN_x$

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compounds. In this work we try to synthesize rare-earth–transition-metal nitrides without using the usual procedure of gas reaction. Compounds with the $\text{Nd}_2\text{Fe}_{14}\text{B}$ -type structure are successfully synthesized by arc melting. The structural and magnetic properties of the $\text{R}_2\text{Fe}_{14}\text{BN}_x$ ($\text{R} = \text{Nd}$ and Sm) compounds are studied by means of x-ray diffraction, neutron diffraction, and AC initial-susceptibility and magnetization measurements.

2. Experimental details

Polycrystalline samples, with starting compositions of $\text{Nd}_2\text{Fe}_{14}\text{BN}_x$ ($x = 0, 0.5, 1.0$) and $\text{R}_2\text{Fe}_{14}\text{BN}$ ($\text{R} = \text{La}, \text{Ce}, \text{Pr}, \text{Sm}, \text{Gd}$ and Er), were prepared by arc melting. Boron and nitrogen were added in the form of Fe–B alloy and boron nitride. The boron nitride was prepared by molecular beam epitaxy (MBE). The as-cast samples were annealed at 950°C for two weeks and then checked by x-ray diffraction. The actual composition of nitrogen in the homogenized samples was determined by a TC-436 oxygen–nitrogen measurement system. The analyses to obtain the nitrogen compositions were performed twice for each sample. One analysis was carried out just after the preparation of the sample. Another was performed after aging the sample for four years.

The neutron diffraction measurements were performed on the powder diffractometer at the heavy-water research reactor at the Institute of Atomic Energy in Beijing [10]. The powder sample was packed in a 0.5 cm diameter and 5 cm high thin-walled cylindrical vanadium cell. The diffraction data were collected at room temperature with a neutron wavelength of 1.184×10^{-2} cm by scanning from 10° to 80° with steps of 0.15° . The diffraction patterns obtained were analysed by means of Rietveld's profile technique [11].

The Curie temperatures of these compounds were determined by AC initial-susceptibility measurements from room temperature up to 450°C . Magnetization measurements up to 6.5 T were performed at 1.5 K and 293 K in an extracting-sample magnetometer at the Institute of Physics of the Chinese Academy of Sciences. The temperature dependence of $\text{Nd}_2\text{Fe}_{14}\text{BN}_x$ was measured by an extracting-sample magnetometer (ESM) and a SQUID magnetometer. Powdered samples of cylindrical shape were used after aligning the powders at room temperature parallel and perpendicular to the cylinder axis in a magnetic field of 1 T and fixing the direction with epoxy resin. The magnetic isotherms at both 1.5 K and 293 K were recorded with the external field either parallel or perpendicular to the alignment field. The anisotropy fields at room temperature were derived from the intersection points of the extrapolated magnetization curves of the parallel- and perpendicular-aligned materials. Values for the saturation magnetization M_s were derived by extrapolating the parallel-magnetization curves to infinite field. The singular-point-detect (SPD) method was also used to determine the anisotropy field by applying an external field of 15 T at room temperature in the High Field Installation at our laboratory. The peak in the second-derivative curves measured by the SPD method corresponds to the anisotropy field of the compound studied.

3. Results and discussion

The x-ray diffraction pattern, shown in figure 1, reveals that the $\text{Nd}_2\text{Fe}_{14}\text{BN}$ alloy studied is essentially single phase with the tetragonal $\text{Nd}_2\text{Fe}_{14}\text{B}$ -type structure. Some minor second phases were almost eliminated by prolonged annealing. $\text{Nd}_2\text{Fe}_{14}\text{BN}_{0.5}$ and $\text{Sm}_2\text{Fe}_{14}\text{BN}$ alloys form in single phases of the tetragonal $\text{Nd}_2\text{Fe}_{14}\text{B}$ -type structure also. This indicates that the compounds with the $\text{Nd}_2\text{Fe}_{14}\text{B}$ -type structure are successfully synthesized by arc melting. Also it means that the bond of boron nitrides can be broken by arc melting, so the boron

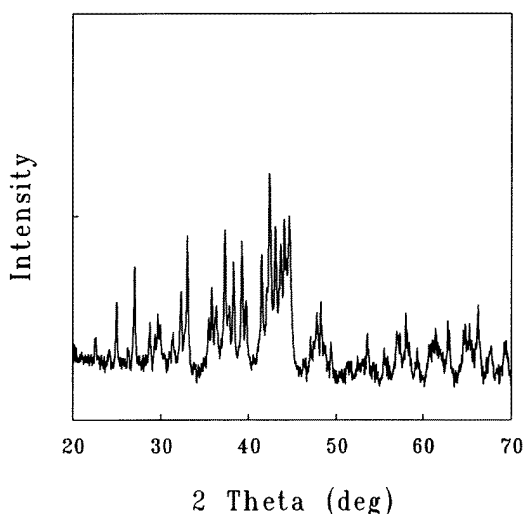


Figure 1. The x-ray diffraction pattern of the compound $Nd_2Fe_{14}BN_{0.1}$.

and nitrogen atoms can form a new compound with other rare-earth and transition-metal atoms. The gas analyses were performed to determine the actual nitrogen compositions in the homogenized samples. It was found that the nitrogen compositions are close to 0.05 and 0.1 atom per unit formula for each compound, corresponding, respectively, to the starting nitrogen compositions of 0.5 and 1.0. This indicates that most of the nitrogen atoms (about 90% of the starting nitrogen atoms) vaporize out of the samples during arc melting. Only about 10% of the nitrogen remains in the compound after arc melting; this may occupy the interstitial site (4f), as when prepared by gas reaction [7], or absorb in the grain boundaries. It should be noted here that the rare-earth–transition-metal boron nitrides synthesized in the present work are stable quaternaries. Since they were made by arc melting, their thermal stability should be comparatively high, so they should not be easy to decompose into RN_x and α -Fe phases at high temperatures. We have performed the gas analyses for each sample using the TC-436 oxygen–nitrogen measurement system twice, separately, just after the preparation of the sample and after aging the sample for four years. The results indicate that the nitrogen atoms have been stable in the samples since the alloys were melted and annealed four years ago.

A neutron diffraction study of the $Nd_2Fe_{14}BN_{0.05}$ compound has been carried out. The observed diffraction lines are interpreted using the nuclear and magnetic coherent scattering. The diffraction patterns of the sample can be indexed in a polyphase program [11]. The boron is in a tetragonal cell (space group $P4_2/mnm$), with parameters $a = 8.810 \text{ \AA}$, $c = 12.24 \text{ \AA}$. The results of the refinement procedure around the main phase, including the coordinates of the crystallographic sites, the occupation of the atoms at these sites, and the magnetic moments are represented in table 1. Although the actual composition for nitrogen is outside the range of validity of the neutron diffraction study, the result confirms that a nearly single phase with tetragonal $Nd_2Fe_{14}B$ -type structure forms, with a small amount of α -Fe (less than 3%).

Nevertheless, nitrogen atoms can be introduced into the $Nd_2Fe_{14}B$ -type lattice by arc melting. A more recent study, using high-resolution transmission electron microscopy (HRTEM), shows the existence of nitrogen inside the lattice of the $Nd_2Fe_{14}B$ -type phase [14]. In the $Nd_2Fe_{14}B$ -type structure, nitrogen atoms ‘prefer’ to occupy the interstitial site (4f).

Table 1. Coordinates of sites, occupations of atoms, and magnetic moments at different sites for the compound $\text{Nd}_2\text{Fe}_{14}\text{BN}_{0.1}$. The experimental errors for the coordinates of the atomic sites, occupations of atoms, and magnetic moments at different sites were estimated to be within ± 0.001 , ± 0.1 , $\pm 0.01 \mu_B$, respectively.

Atom (site)	<i>x</i>	<i>y</i>	<i>z</i>	Number of atoms	$\mu_z (\mu_B)$
Nd (4f)	0.256	0.256	0.000	4.0	2.93
Nd (4g)	0.147	-0.147	0.000	4.0	1.28
Fe (16k ₁)	0.224	0.569	0.123	16.0	2.31
Fe (16k ₂)	0.039	0.355	0.175	16.0	2.35
Fe (8j ₁)	0.0991	0.0991	0.206	8.0	2.29
Fe (8j ₂)	0.316	0.316	0.250	8.0	2.56
Fe (4e)	0.500	0.500	0.118	4.0	2.56
Fe (4c)	0.000	0.500	0.000	4.0	2.21
B (4g)	0.358	-0.358	0.000	4.0	0.00
N (4f)	0.316	0.316	0.000	0.4	0.00

Table 2. Lattice parameters (derived from x-ray diffraction), Curie temperatures, saturation magnetizations, and anisotropy fields of the compounds $\text{R}_2\text{Fe}_{14}\text{BN}_x$ with $\text{R} = \text{Nd}$ and Sm . The two columns for the anisotropy fields were derived from the intersection points of the extrapolated magnetization curves and the SPD curves, respectively. The data for $\text{Nd}_2\text{Fe}_{14}\text{B}$ and $\text{Sm}_2\text{Fe}_{14}\text{B}$ were also taken from reference [3]. The experimental errors for the lattice parameters, Curie temperatures (T_c), magnetizations (M_s), and anisotropy fields (B_A) were estimated to be within $\pm 0.01 \text{ \AA}$, $\pm 1 \text{ K}$, $\pm 1 \text{ A m}^2 \text{ kg}^{-1}$, and $\pm 0.1 \text{ T}$, respectively.

Compounds	Lattice parameters		T_c (K)	M_s (1.5 K)		B_A (293 K)	
	<i>a</i> (Å)	<i>c</i> (Å)		($\text{A m}^2 \text{ kg}^{-1}$)	($\mu_B/\text{f.u.}$)	(T)	(T)
$\text{Nd}_2\text{Fe}_{14}\text{B}$	8.79	12.15	586	190	37.7	7.3	8.1
$\text{Nd}_2\text{Fe}_{14}\text{BN}_{0.05}$	8.78	12.18	590	180	35.0	10.7	8.8
$\text{Nd}_2\text{Fe}_{14}\text{BN}_{0.1}$	8.79	12.20	596	175	34.4	10.3	8.8
$\text{Sm}_2\text{Fe}_{14}\text{B}$	8.80	12.15	616	168	33.3	15.0	—
$\text{Sm}_2\text{Fe}_{14}\text{BN}_{0.1}$	8.79	12.20	584	168	33.3	10.5	8.5

According to a rigid-model calculation, there is enough space for the (4f) interstices to contain nitrogen atoms. Furthermore, the difference of electronegativity between nitrogen and rare-earth atoms is greater than that between nitrogen and the other atoms. Evidently, the nitrogen atoms have a tendency to take positions adjacent to the rare-earth ions so as to keep the energy lower, which would be the main reason for nitrogen atoms to occupy the (4f) interstitial sites preferentially. This is in good agreement with the results obtained for the nitrides $\text{R}_2\text{Fe}_{14}\text{BN}_x$ ($\text{R} = \text{Y}, \text{Nd}$) prepared by gas reaction [8, 12].

The main phase of $\text{R}_2\text{Fe}_{14}\text{BN}$ alloys with $\text{R} = \text{Y}, \text{La}, \text{Ce}, \text{Pr}, \text{Gd}, \text{Dy},$ and Er is of the tetragonal $\text{Nd}_2\text{Fe}_{14}\text{B}$ type, but with larger amounts of the minor phases R_2Fe_{17} and $\alpha\text{-Fe}$. So we do not study the magnetic properties of these compounds in the present paper. A further procedure is being carried in order to prepare single phases of these compounds by controlling the arc melting and the annealing procedures. Nevertheless, the formation of the main phase of the tetragonal $\text{Nd}_2\text{Fe}_{14}\text{B}$ type confirms also that the bond of boron nitrides can be broken by arc melting to allow combination with rare-earth and transition-metal atoms.

The curves of the ac initial susceptibilities of $\text{Nd}_2\text{Fe}_{14}\text{BN}_x$ ($x = 0, 0.05, 0.1$) compounds from room temperature to $450 \text{ }^\circ\text{C}$ are given in figure 2. The results of the magnetization measurements, recorded by the ESM at 1.5 K and 293 K, for the $\text{Nd}_2\text{Fe}_{14}\text{BN}_{0.05}$, $\text{Nd}_2\text{Fe}_{14}\text{BN}_{0.1}$, and $\text{Sm}_2\text{Fe}_{14}\text{BN}_{0.1}$ compounds are shown in figures 3–5, respectively. The anisotropy fields at room temperature, derived from the intersection points of the extrapolated magnetization

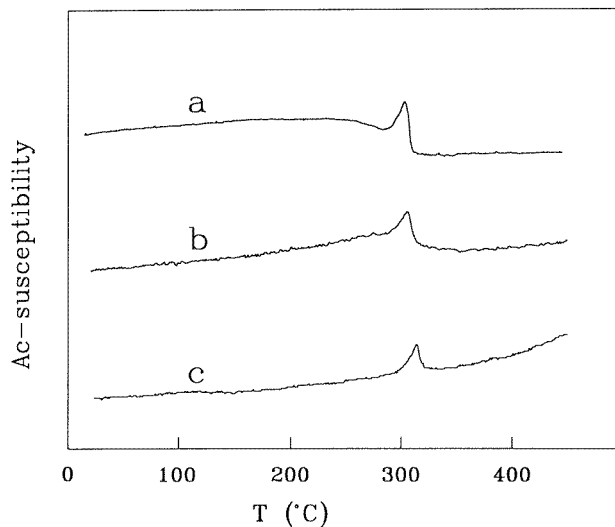


Figure 2. AC initial susceptibilities of the compounds (a) $Nd_2Fe_{14}B$, (b) $Nd_2Fe_{14}BN_{0.05}$, and (c) $Nd_2Fe_{14}BN_{0.1}$.

curves, for the $Nd_2Fe_{14}BN_{0.05}$ and $Nd_2Fe_{14}BN_{0.1}$ compounds are 10.7 T and 10.3 T respectively. The SPD curve at room temperature of $Nd_2Fe_{14}BN_{0.1}$ is given in figure 6, which actually corresponds to $-d^2M/dB^2$. The anisotropy fields, derived from the SPD curves, for both $Nd_2Fe_{14}BN_{0.05}$ and $Nd_2Fe_{14}BN_{0.1}$ compounds are equal to 8.8 T. It is obvious that the room temperature anisotropy fields of the boron nitrides are slightly larger than that of $Nd_2Fe_{14}B$ [1–4, 13]. The lattice parameters (derived from x-ray diffraction), Curie temperatures, saturation magnetizations, and anisotropy fields of the boron nitrides are listed in table 2. From table 2, it is seen that addition of nitrogen atoms obviously does not expand the lattice of the $Nd_2Fe_{14}B$ compound, due to the fact that only a few nitrogen atoms remain in the samples. Consequently, the effect on the increase of the Curie temperature of such addition is not very evident, compared with that caused by gas reaction [8]. However, the slight increase of the Curie temperature suggests that a small amount of nitrogen might be introduced into the lattice of the $Nd_2Fe_{14}B$ phase. The Curie temperatures and anisotropy fields at room temperature of the $R_2Fe_{14}B$ compounds are slightly increased by the incorporation of nitrogen. The addition of the nitrogen atoms gives a weak (strong) negative effect on the saturation magnetization at 4.2 K (at 293 K) for $Nd_2Fe_{14}B$. Comparing the magnetization isotherms measured at 1.5 K and 293 K shown in figures 3 and 4, one sees that the easy-cone structure at low temperature of $Nd_2Fe_{14}B$ persists for the Nd-containing boron nitrides, suggesting that a spin reorientation (SR) exists as reported for $Nd_2Fe_{14}B$. Illustration of the presence of the first-order magnetization processes requires application of a higher magnetic field at low temperatures. The temperature dependences of the magnetizations, measured by the ESM at 6.5 T, of $Nd_2Fe_{14}BN_{0.05}$, $Nd_2Fe_{14}BN_{0.1}$, and $Sm_2Fe_{14}BN_{0.1}$ are represented in figure 7. The temperature dependence of the magnetization, measured by the SQUID at 0.03 T, of $Nd_2Fe_{14}BN_{0.1}$ is presented in the inset of figure 7. The inset shows that in $Nd_2Fe_{14}BN_{0.1}$ a SR transition occurs at 135 K which is also the case for $Nd_2Fe_{14}B$ [3, 4]. The SR is also found to occur at the same temperature in $Nd_2Fe_{14}BN_{0.05}$.

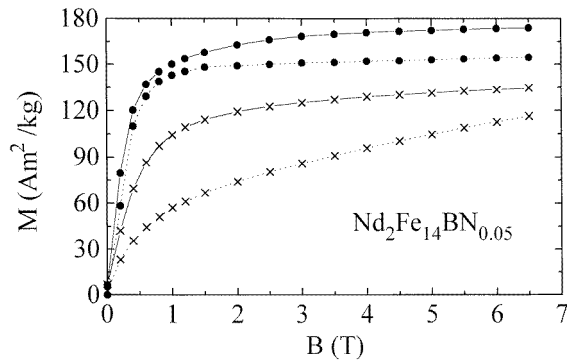


Figure 3. Magnetization curves with the magnetic field direction perpendicular (\times) and parallel (\bullet) to the aligned direction for the compound $\text{Nd}_2\text{Fe}_{14}\text{BN}_{0.05}$ at 1.5 K (solid curves) and 293 K (dotted curves).

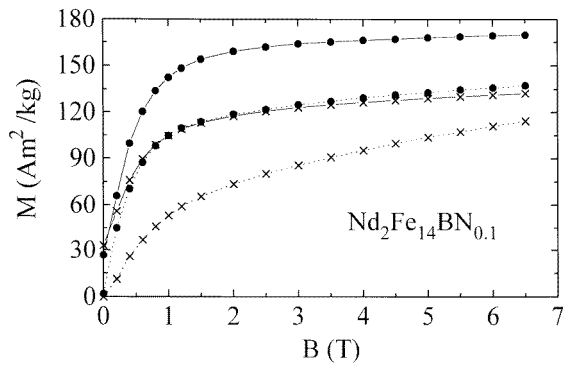


Figure 4. Magnetization curves with the magnetic field direction perpendicular (\times) and parallel (\bullet) to the aligned direction for the compound $\text{Nd}_2\text{Fe}_{14}\text{BN}_{0.1}$ at 1.5 K (solid curves) and 293 K (dotted curves).

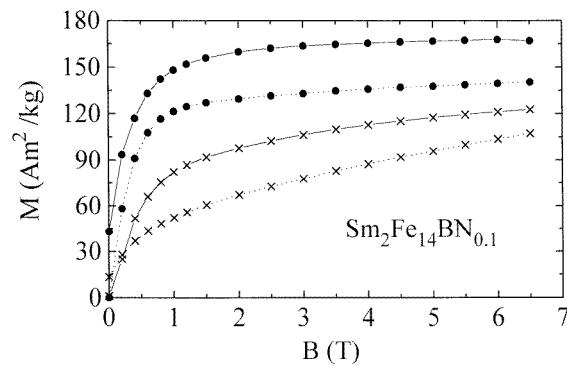


Figure 5. Magnetization curves with the magnetic field direction perpendicular (\times) and parallel (\bullet) to the aligned direction for the compound $\text{Sm}_2\text{Fe}_{14}\text{BN}_{0.1}$ at 1.5 K (solid curves) and 293 K (dotted curves).

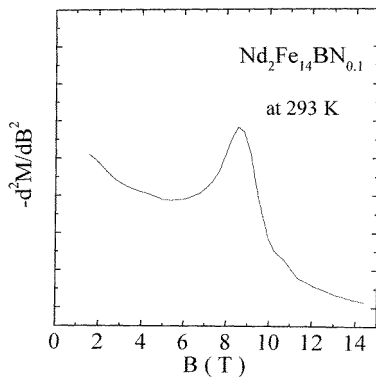


Figure 6. The SPD curve at room temperature of the compound $Nd_2Fe_{14}BN_{0.1}$.

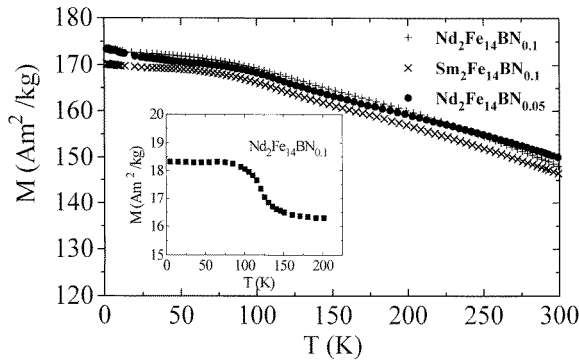


Figure 7. The temperature dependence of the magnetization measured at 6.5 T for the compounds $Nd_2Fe_{14}BN_{0.05}$ (●), $Nd_2Fe_{14}BN_{0.1}$ (+), and $Sm_2Fe_{14}BN_{0.1}$ (×). The inset shows the temperature dependence of the magnetization measured at 0.03 T for the compound $Nd_2Fe_{14}BN_{0.1}$.

In recent work, we investigated the structure and magnetic properties of $Nd_2Fe_{14}B$ -based alloys prepared by mechanical alloying (MA) with either raw or milled BN powders. $Nd_2Fe_{14}BN_x$ phases with x up to 0.25 are found to coexist with amounts of NdN and α -Fe in the MA and annealed samples. Coercivities as high as 20 kOe are achieved for the MA $Nd_2Fe_{14}BN_x$ -based alloy. In reference [8], it was reported that the Curie temperature of the compound $Nd_2Fe_{14}BN_{0.5}$, prepared by gas reaction, is about 50 °C higher than that of the pure compound $Nd_2Fe_{14}B$. On the basis of these facts and the assumption of a linear nitrogen dependence of the Curie temperature, we found that the composition of the $Nd_2Fe_{14}B$ -based hard magnetic phase made by MA can be close to $Nd_2Fe_{14}BN_{0.25}$ [8]. The results in this work support this assumption. It can be seen from table 2 that the Curie temperature of $Nd_2Fe_{14}BN_x$ depends linearly on the composition, from the results of AC susceptibility measurements and the gas analyses. The slight increase of the Curie temperature indicates that a small amount of nitrogen is introduced into the lattice of the $Nd_2Fe_{14}B$ phase during arc melting.

In conclusion, the quaternary rare-earth–transition-metal boron nitrides $Nd_2Fe_{14}BN_{0.05}$, $Nd_2Fe_{14}BN_{0.1}$, and $Sm_2Fe_{14}BN_{0.1}$ have been synthesized by arc melting. The bond of the boron nitrides can be broken by arc melting to allow combination with rare-earth and transition-metal atoms. The structure and magnetic properties of these quaternary compounds have been studied. The Curie temperature and magnetic anisotropy of the compound $Nd_2Fe_{14}B$ are slightly enhanced by introducing nitrogen into the lattice of $Nd_2Fe_{14}B$, indicating that a small

quantity of nitrogen has been added into the lattice of the hard $\text{Nd}_2\text{Fe}_{14}\text{B}$ phase during arc melting. The SR transition temperature of $\text{Nd}_2\text{Fe}_{14}\text{BN}_{0.1}$ is the same as that of $\text{Nd}_2\text{Fe}_{14}\text{B}$. The present work has developed a new method of synthesizing quaternary rare-earth-transition-metal boron nitrides. We have also shown that the boron nitrides could be used as a starting materials for synthesizing rare-earth-transition-metal compounds and/or permanent magnets.

Acknowledgments

This work was partly supported by the National Natural Science Foundation of China under grant No 59725103 and by the Committee of Sciences and Technology of Shenyang and Liaoning. We thank Professors Zhang Bai-sheng, Yang Ji-lian, and Du Hong-lin of the Institute of Atomic Energy, Beijing, and Professor Fan Shi-yong of the Institute of Physics, Academia Sinica, for their help in performing the neutron diffraction and measuring the magnetizations, respectively.

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