論文 **Original Paper**

Boron Nonstoichiometry, Hardness and Magnetic Properties of the Perovskite-Type Gadolinium Rhodium Boride

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Abstract: Samples of $GdRh_3B_x$ were synthesized using the arc-melting method. A compound of $GdRh_3B_x$ has a perovskite-type cubic structure (space group: Pm3m) in which the concentration of boron is distributed between x = 1.000 (20 at%B) and 0.444 (10 at%B) for $GdRh_3B_x$. The lattice parameter a of $GdRh_3B_x$ depends on x and varies almost linearly from a = 0.41831(6)nm (x = 1.000) to 0.4121(1)nm (x = 0.444). The Vickers microhardness of $GdRh_3B_x$ increases with increasing B content in the range of x = 0.444～1.000, and hardness of the $GdRh_3B_{0.444}$ and $GdRh_3B_{1.000}$ is 3.4(±0.12) and 6.8(±0.08)GPa, respectively. The stoichiometric compound $GdRh_3B$ has a ferromagnetic property with the Curie temperature of 14 K.

Keywords: $GdRh_3B$; Perovskite-type compound; Nonstoichiometry; Hardness; Magnetic property

1. Introduction

Rare-earth ternary borides have attracted attention due to the interest in their properties of the competitions between the properties of magnetism and superconductivity. Currently, three different types of compounds, RRh_3B, RRh_3B_2 and RRh_4B_4 of the system of R–Rh–B (R = rare earth) have been reported. Recently, rare earth rhodium borides RRh_3B with a cubic perovskite-type structure have been investigated by many researchers.[1–8] We have already reported on the growth and crystal structure of $GdRh_3B$ single crystals.[5] However, there is no report on the properties of stoichiometric $GdRh_3B$ or on the data of the boron nonstoichimetry range x of boron in $GdRh_3B_x$.

This paper deals with the synthesis of the perovskite-type $GdRh_3B_x$ compound using the arc-melting method. Chemical analysis of each sample were performed. The nonstoichiometry range of boron in the compound is clarified by X-ray diffraction (XRD) analysis. The variation of the lattice constant of the samples is investigated as a function of the boron concentration x in $GdRh_3B_x$. The relationship between the Vickers microhardness and boron concentration x in $GdRh_3B_x$ is studied. Magnetic properties of the stoichiometric $GdRh_3B$ are also reported. The nature of the chemical bonding in this ternary boride is discussed.

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2. Experimental

Polycrystalline samples of $GdRh_3B_x$ were prepared from the high-purity elements by conventional arc-melting and annealing techniques. 99.9% pure Gd, Rh and 99.8% pure B were used as starting materials. They were weighed in the atomic ratio 1 : 3 : x, where x = 1.000 (20 at%B), 0.706 (15 at%B), 0.444 (10 at%B) and 0.210 (5 at%B). The starting materials, 2 g of each sample, were placed in a water-cooled copper hearth in a reaction chamber. Argon was used as a protective atmosphere. The pressure inside the chamber was approximately 1 atm.

A small amount of residual oxygen in argon was eliminated by fusing a button of titanium as a reducing agent. The starting materials were then melted by an argon arc plasma flame. A dc power source with 20 V and 100 A was used for 3 min. Arc-melting was performed 3 times for each sample. All of the arc-melting synthesized samples reveal a silvery metallic luster. They were wrapped in tantalum foil and annealed at 1573 K for 24 h under vacuum to ensure homogeneity.

The samples were fused using $NaHSO_4$ as a flux, and then the obtained matter was dissolved into HCl. The chemical composition of each solution was analyzed by the inductively coupled plasma atomic emission spectrometry (ICP–AES) method. Zn was used as an internal standard. Chemical analysis determined that the chemical compositions of the samples almost corresponded to the atomic ratio of the starting compositions.

The Vickers microharduess of the samples was meas-

ured at room temperature in the same manner as in ref. 9. A load of 200 g was applied for 15 s and at least 7 impressions were recorded for each sample. Obtained values were averaged and the experimental error was estimated.

Magnetic properties of the stoichiometric compound $GdRh_3B$ were measured with a pendulum-type magnetometer in the temperature range from 4.7 K to 300 K.

3. Results and discussion

Chemical analysis determined that the chemical compositions of the samples almost corresponded to the atomic ratio of the starting compositions. Structural characterization of the samples was performed by XRD. The compound of $GdRh_3B_x$ has a perovskite-type cubic structure (space group: Pm3m). Figure 1 shows the arrangement of atoms in perovskite-type $GdRh_3B$. Large black, large gray and small black circles represent Gd, Rh and B atoms, respectively. The nonstoichiometry of B in the compound was investigated. Figure 2 shows XRD profiles for $GdRh_3B_x$. Figure 3 shows the variation of lattice parameter a with boron concentration x in $GdRh_3B_x$ compounds. The concentration of boron is distributed between x = 1.000 (20 at %B) and 0.444 (10 at%B) for $GdRh_3B_x$.

The solid solution range of B in $GdRh_3B_x$ is in good agreement with those reported for $ErRh_3B$[5] and YRh_3B.[8] Lattice parameter a of $GdRh_3B_x$ depends on x, and varies linearly from a = 0.4121(1)nm (x = 0.444) to 0.41831(6)nm (x = 1.000). Thus the addition of boron has resulted in the extreme expansion of the cubic lattice. Lattice parameters of $GdRh_3B_x$ are given in Table I. Interstitial solid solution, the insertion of 'foreign' ions or atoms into metals, is well known. In particular, the insertion of nonmetal elements (H, B, C, N, O) into transition metals is extensively reported. As in the case of C into γ–Fe (fcc), the increasing the concentration of 'foreign' ions or atoms enlarge the lattice of the parent materials. For the case of the fcc structure, the size of the octahedral vacant is larger than that of the

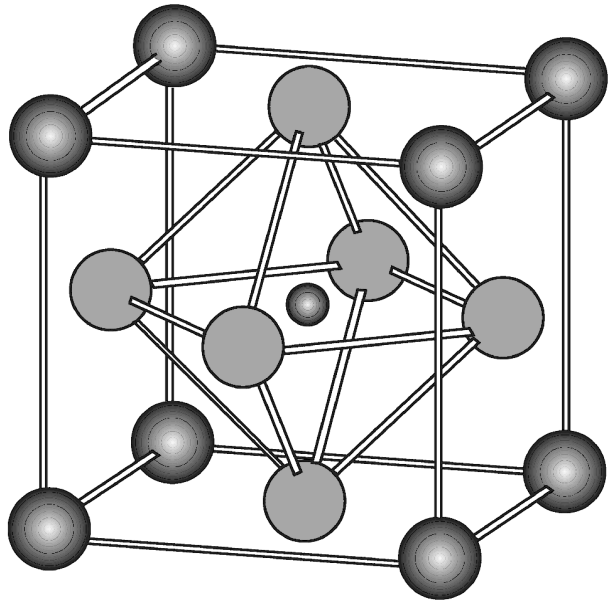

Fig. 1 Arrangement of atoms in the perovskite-type $GdRh_3B$. Large black, large gray and small black circles represent Gd, Rh and B atoms, respectively.

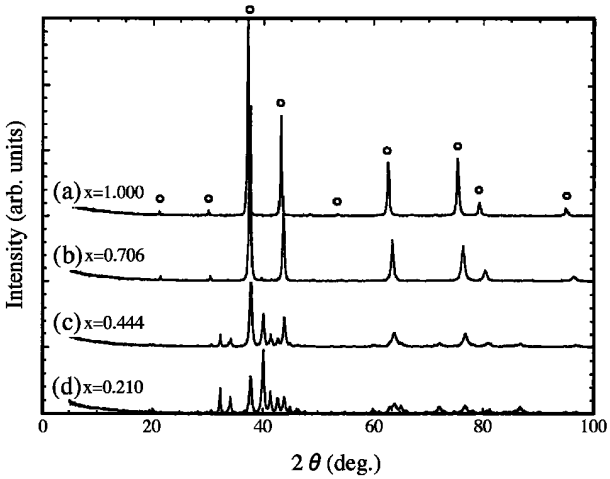

Fig. 2 XRD profiles for $GdRh_3B_x$ with x = 1.000 (a), x = 0.706 (b), x = 0.444 (c) and x = 0.210 (d).

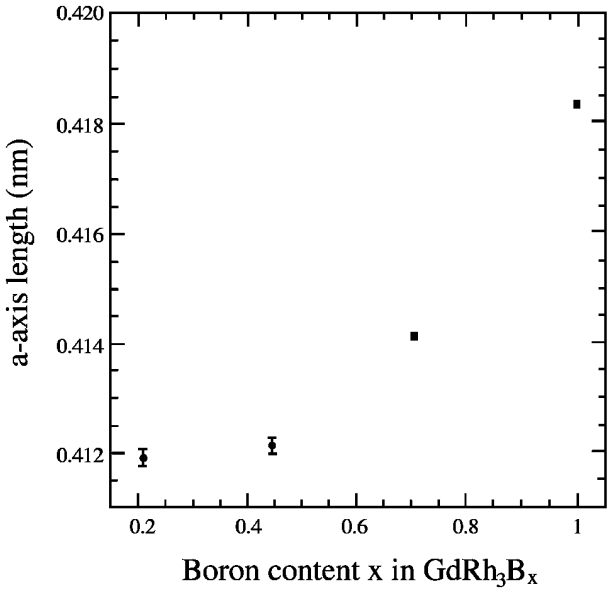

Fig. 3 The variation of lattice constant a as a function of boron concentration x in $GdRh_3B_x$.

Table I Lattice parameter of $GdRh_3B_x$

Sample	Lattice parameter
(atomic% of boron)	a, nm
$GdRh_3B_{1.000}$(20)	0.41831(6)
$GdRh_3B_{0.706}$(15)	0.41410(6)
$GdRh_3B_{0.444}$(10)	0.4121(1)
$GdRh_3B_{0.210}$(5)	0.4119(2)

tetrahedral one. Therefore, the 'foreign' ions or atoms enter the octahedral vacant site. These rules can be applied to the title compound of $GdRh_3B$. That is, 'foreign' B atoms enter into the octahedral vacant site. Increasing the concentration of B atoms enlarges the size of the lattice constants. However, there are some properties which differ from these rules. We would like to emphasize that $GdRh_3B_x$ is an unconventional compound. The Rh–B length is 10 % shorter and the Gd–Rh length is 5 % shorter than the summation of atomic radii. When we consider this property, combine with the absence of $x=0$, we can say that $GdRh_3B_x$ is not a conventional interstitial solid solution. Boron acts, not only to enter the vacant site, but also to stabilize the perovskite structure, attracting Rh as the center of the cluster forming the $B–Rh_6$ octahedron. This type of B insertion is considered to be the key to stabilize this system.

The Vickers mirohardness of $GdRh_3B_x$ increases with increasing B content in the range of $x=0.444\sim1.000$, and hardness of $GdRh_3B_{0.444}$ and $GdRh_3B_{1.000}$ is 3.4($\pm$0.12) and 6.8($\pm$0.08)GPa, respectively. Figure 4 shows the Vickers hardness for $GdRh_3B_x$ as a function of the boron content, x. The values of the Vickers hardness for $GdRh_3B_x$ is given in Table II. Data in the literature on the binary compounds Rh_7B_3 and RhB are also listed.[10]

$GdRh_3B$ shows the ferromagnetic property. The magnetization (M) vs. the temperature (T) curve below 30 K in a magnetic field of 10 kOe and the inverse susceptibility ($1/\chi$) vs. the temperature curve in a magnetic field of 5.85 kOe from 20 K to 300 K are shown in Figs. 5 and 6. The $1/\chi$ vs the T curve follows the Curie-Weiss law, and from the linear line, the paramagnetic Curie point (θ_p) and the effective Bohr magneton number (μ_{eff}) are also obtained to be $\theta_p=11$ K and $\mu_{eff}=7.90(\mu_B)$, respectively. The Curie temperature (T_c) is determined from the linear relation between M^2 and T just below T_c in a magnetic field of 1.0 kOe to be $T_c=14$ K. The value of μ_{eff} is nearly equal to that

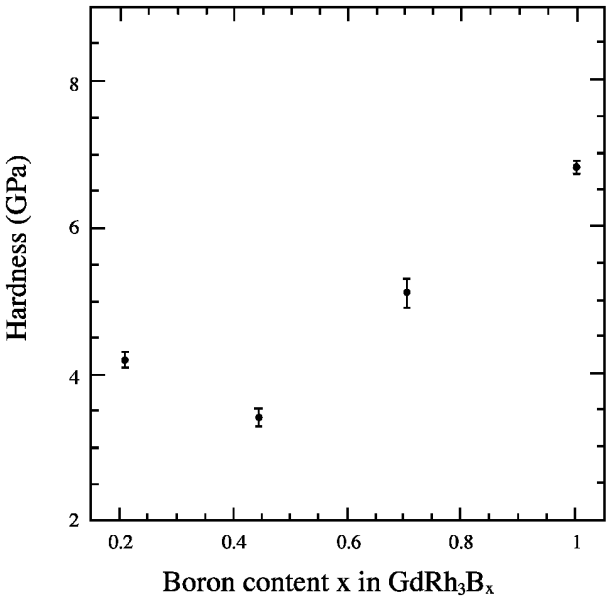

Fig. 4 Vickers microhardness for $GdRh_3B_x$ as a function of the boron content, x.

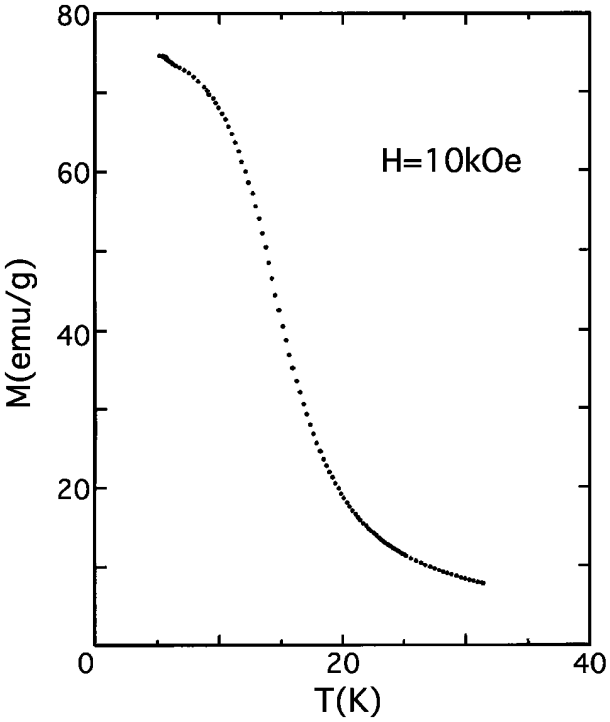

Fig. 5 Magnetization vs temperature T for $GdRh_3B$. ($H=10$ kOe)

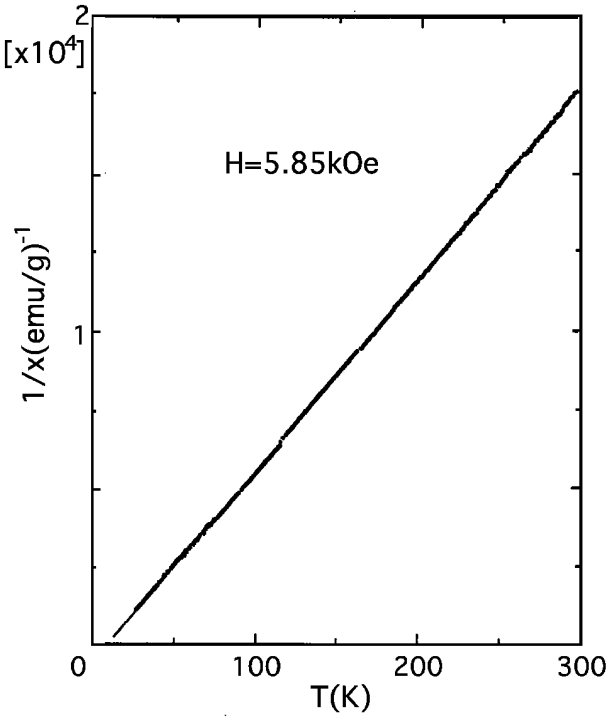

Fig. 6 Inverse magnetic susceptibility vs temperature T for $GdRh_3B$. ($H=5.85$ kOe)

Table II Vickers hardness of the $GdRh_3B_x$

Sample (atomic% boron)	Hardness, GPa	Reference
$GdRh_3B_{1.333}$(25)	7.2(±0.09)	This work
$GdRh_3B_{1.000}$(20)	6.8(±0.08)	This work
$GdRh_3B_{0.706}$(15)	5.1(±0.20)	This work
$GdRh_3B_{0.444}$(10)	3.4(±0.12)	This work
$GdRh_3B_{0.210}$(5)	4.2(±0.10)	This work
RhB*(50)	12.13	10)
Rh_7B_3**(30)	7.77	10)

* hexagonal-type structure
** hexagonal-type structure

of the free electron Gd^{3+} ion and the magnetic moment in a magnetic field of 17.8 kOe at 4.7 K is $\mu_s = 6.4(\mu_B)$, about 10% smaller than that of the full magnetic moment value 7.0 (μ_B) of Gd.

4. Conclusion

Compound of $GdRh_3B_x$ was synthesized by the arc-melting method; $GdRh_3B_x$ has a perovskite-type cubic structure (space group: Pm3m). Boron nonstoichiometry ranged between x = 1.000 (20 at%B) and 0.444 (10 at%B) for $GdRh_3B_x$. The lattice parameter a of $GdRh_3B_x$ depends on x and varies almost linearly from $a = 0.41831(6)$nm (x = 1.000) to 0.4121(1)nm (x = 0.444). The hardness of $GdRh_3B_x$ increases with increasing B content in the range of $x = 0.444 \sim 1.000$, and hardness of the $GdRh_3B_{0.444}$ and $GdRh_3B_{1.000}$ is 3.4(±0.12) and 6.8(±0.08)GPa, respectively. The $GdRh_3B$ behaves ferromagnetic with the Curie temperature of 14 K.

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