Original Paper

Synthesis, Boron Solubility and Properties of Perovskite-Type Rare Earth Palladium Borides

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Polycrystalline samples of RPd_3B_x (R = La, Gd, Lu, Sc) were successfully synthesized by the arc melting method. RPd_3B_x compounds have a perovskite-type cubic structure. The solid solution range of RPd_3B_x was clarified. Magnetism, Vickers microhardness and thermochemical properties of RPd_3B_x were also reported.

Key Words: *RPd_3B_x*, *Perovskite-Type Compound*, *Nonstoichiometric Boride*, *Magnetism*, *Microhardness*, *Oxidation Resistance*

1. Introduction

The ternary systems R-M-B (R = rare earth element; M = platinum group element) reveal a variety of crystal structures, and these ternary borides have received considerable attention from many researchers in the fields of crystallography, magnetism, superconductivity, heavy-electron, valence fluctuation and catalyzers [1-9]. Recently, we have been intensively investigating rare earth rhodium borides RRh_3B_x with respect to the high stability of perovskite-type borides [10-15]. In the present paper, we introduce the successful synthesis of the perovskite-type RPd_3B_x by the arc melting method. In this experiment, among the rare earth elements, we focused on La, Gd, Lu and Sc. La, Gd and Lu are the smallest, middle and the largest atomic number of the lanthanides, respectively. Sc located in the fourth row and the third column in the periodic table; it has too small atomic number as compared with the lanthanides. The solid solution range of boron in the RPd_3B_x was clarified by X-ray diffraction (XRD) analysis, and the change of the lattice constant of the samples was investigated as a function of the boron concentration x. Then, magnetic properties were studied for the samples. From the viewpoint of applications that utilize the hardness of boride, we investigated the dependence of the hardness of RPd_3B_x on the amount of B. For catalyst applications, we were interested in the thermochemical stability of RPd_3B_x. To investigate the thermochemical stability, we heated RPd_3B_x to a high temperature in the atmosphere using a thermogravimetric (TG) analysis and differential thermal analysis (DTA).

2. Experimental details

2.1 Sample preparation

Samples of RPd_3B_x were synthesized by the arc melting method using 99.9 % pure R (La, Gd, Lu, Sc), Pd and 99.8 % pure B as raw materials. The starting materials were into an atomic ratio of 1 : 3 : x, where x = 0 (0 mass% B), 0.210 (5 mass% B), 0.444 (10 mass% B), 0.706 (15 mass% B) and 1.000 (20 mass% B). The mixture approximately 2 g for 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 reaction chamber was approximately 1 atm. A small amount of residual oxygen in

argon was eliminated by fusing a button of titanium as a reducing reagent. The starting materials were then melted by an argon arc plasma flame. A DC power source of 20 V and 100 A was applied for 3 min. Arc-melting was performed three times for each sample. Finally, synthesized samples were wrapped in tantalum foil and annealed at 1573 K for 24 h in vacuum to ensure homogeneity.

2.2 Characterization

The chemical composition of each sample was analyzed by induction coupled plasma atomic emission spectrometry (ICP-AES) method. Structural characterization of the samples was performed by the means of XRD at room temperature. The magnetic susceptibility measurements were performed by using a commercial SQUID magnetometer (Quantum Design Inc., MPMS-XL5). The Vickers microhardness (HV_m) for the samples was measured at room temperature as described in Ref. [16,17]. Ten points of each sample were measured with applied load of 100 g for 15 s. The obtained values were averaged and the experimental error was estimated. TG-DTA measurement was performed between room temperature and 1473 K in order to investigate the oxidation resistivity of the samples in air. A sample of approximately 25 mg was heated at a rate of 10 K·min^{-1} to 1473 K. The oxidation products were analyzed by powder XRD.

3. Results and Discussion

Polycrystalline samples of RPd_3B_x, which consists of a reactive R and high-melting point B and Pd elements, were successfully synthesized by the arc melting method. All of the synthesized samples had a silvery metallic luster. As the result of chemical analyses, the chemical compositions of the obtained samples approximately corresponded to the atomic ratio of the starting compositions. Evaporation of each element during arc melting synthesis was negligible. In addition, there was no evidence of pollution from the electrode (W) or the hearth (Cu) by the arc melting method.

3.1 Solid solution range of boron

In the unit cell of the cubic RPd_3 (R = La, Gd, Lu, or Sc), the eight corners are occupied by R and the face center is occupied by Pd, while the body center is vacant. RPd_3 can be regarded as having a perovskite structure, which lacks any body center atoms. By varying R, therefore, we estimated the B solubility limit x of RPd_3B_x to determine how much boron (B) would dissolve into the body center.

The solid solution range of boron is investigated. Figure 1 shows the XRD patterns for samples of $GdPd_3B_x$. The boron concentration of x was varied as 0, 0.210, 0.444, 0.706 and 1.000 ; x = 0, 0.210, 0.444, 0.706 and 1.000 in $GdPd_3B_x$ corresponds to mass% B of 0, 5, 10, 15 and 20, respectively. An impurity phase did not coexist with the perovskite-type phase for any boron concentration, x. In the case of $GdPd_3B_x$, for example, the lattice constant does not change when x is increased beyond 0.45. We consider that excess B exists in a composition having a value of x of over 0.45. Excess B does not appear in powder X-ray diffraction pattern because it is amorphous due to the arc melting heat.

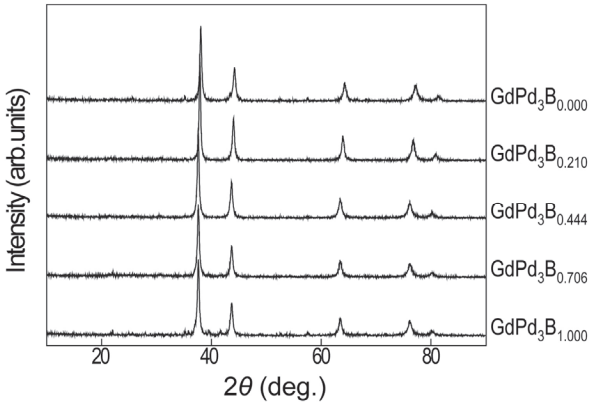

Fig.1 X-ray diffraction patterns for $GdPd_3B_x$ (x = 0, 0.210, 0.444, 0.706 and 1.000); x = 0, 0.210, 0.444, 0.706 and 1.000 in $GdPd_3B_x$ corresponds to mass percentages of B of 0, 5, 10, 15 and 20, respectively.

Figure 2 shows the diffraction patterns for $RPd_3B_{0.444}$ (R = La, Gd, Lu, Sc). In the case of $ScPd_3B_{0.444}$, a small amount of impurity phase was detected. Figure 3 shows the variation of the lattice constant, a as a function of boron concentration in the cubic system of RPd_3B_x. The lattice expansion with increasing boron concentration, x in the compound supports the solid solution range of boron in RPd_3B_x. The solid solution ranges of $GdPd_3B_x$, $LuPd_3B_x$ and $ScPd_3B_x$ are $0 \le x \le 0.45$, $0 \le x \le 0.5$ and $0 \le x \le 0.3$, respectively. The lattice constant a varies linearly in these region. In the case of $LaPd_3B_x$, lattice shrinkage is observed in the range of $0 \le x \le 0.2$. The relationship between the amount of B in $GdPd_3B_x$ and the lattice constant is similar to previously reported relationships [18]. However, our interpretation differs completely

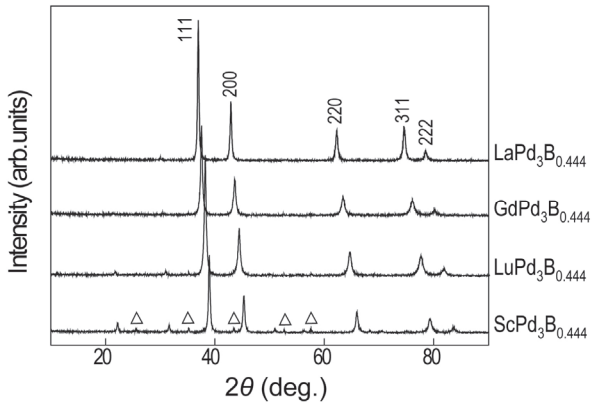

Fig.2 X-ray diffraction patterns for RPd_3B_x (x = 0.444).

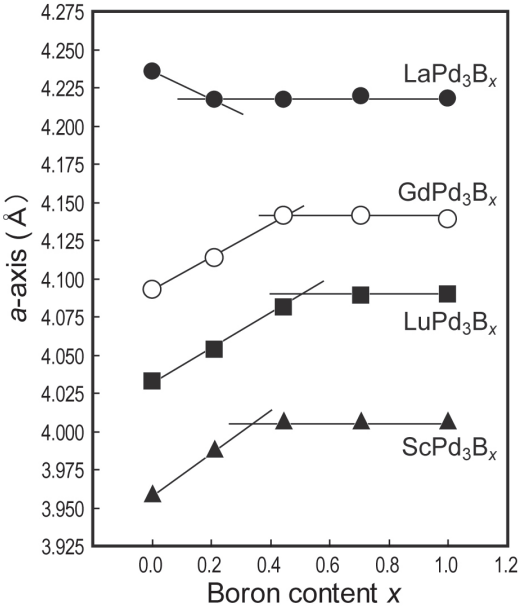

Fig.3 Variation of lattice constant a as a function of boron concentration x in cubic structure RPd_3B_x.

from the past report in which the B solubility limit x was assumed to be 1.

In the case of RPd_3 (x = 0), it has an $AuCu_3$ type structure, and its space group is $Pm3m$. The crystal structure of the compound which has boron introduced into RPd_3 is essentially a cubic system. The exact space group for RPd_3B_x is currently being investigated.

3.2 Magnetism

Figure 4 shows the temperature dependence of the magnetic susceptibility χ of RPd_3B in a magnetic field of 0.5 T. Temperature independent χ observed in RPd_3B (R = La, Lu, Sc) indicates Pauli paramagnetism. Small upturn of χ at low temperatures may result from defects and/or small amount of impurities in the polycrystalline samples. On the other hand, $GdPd_3B$ shows a paramagnetic behavior, which follows the Curies law $\chi = C/T$ where C is the Curie constant. We plotted the inverse susceptibility of $GdPd_3B$ as a function of the temperature. The extrapolation of $1/\chi$ at T = 0 K is almost zero, which indicates the Curie paramagnetism in $GdPd_3B$. The value of the effective Bohr magneton can be roughly evaluated as p = 7.6 from the slope of the linear dependence. The observed value is consistent with the value p = 7.9 of free Gd^{3+} ions. Therefore we conclude that the Curie paramagnetism of $GdPd_3B$ arises from the Gd^{3+} ions.

3.3 Microhardness

We are interested in one of the important mechanical functions of microhardness of borides, because hardness essentially reflects the nature of the chemical bonding of the compound. Figure 5 shows the Vickers microhardness, HV_m as a function of boron concentration x for RPd_3B_x. The HV_m for the RPd_3B_x is distributed over 3.5-7.5 GPa. For example, the value of the micro hardness was 5.4 ± 0.3 GPa, 7.3 ± 0.3 GPa, 3.9 ± 0.2 GPa, 3.8 ± 0.1 GPa and 4.0 ± 0.3 GPa for $GdPd_3B_0$, $GdPd_3B_{0.21}$, $GdPd_3B_{0.444}$, $GdPd_3B_{0.706}$ and $GdPd_3B_{1.000}$, respectively. In the cases of R = La and Gd, the relationship between the hardness and x shows characteristic behavior. The maximum value exists in the vicinity of x = 0.2.

3.4 Oxidation resistance in air

Figure 6 shows TG-DTA curves for $GdPd_3B_x$. According to the DTA analysis, two exothermic peaks were observed at maximum temperatures of 907 K and 990 K for $GdPd_3B_{0.444}$. The increase in the weight due to oxidation was 7.8 %. The oxidized product is a mixture of Pd, $GdBO_3$ and Gd_2O_3. The oxidation onset temperature, weight gain and oxidation product from TG-DTA measurements for the $GdPd_3B_x$ are summarized in Table 1. Similar results was obtained for another RPd_3B_x (R = La, Lu, Sc).

We intend to publish another report that compares the results of our previous studies on RRh_3B_x with the results of this study on RPd_3B_x.

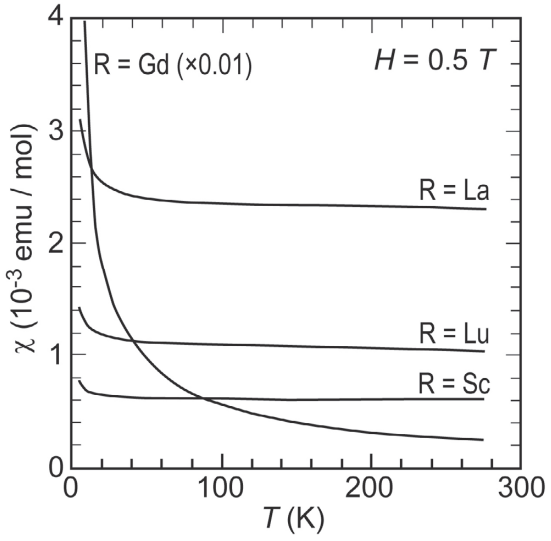

Fig.4 Temperature dependence of the magnetic susceptibility of RPd_3B in H = 0.5 T. It is noted that x of $GdPd_3B$ is plotted after being reduced one hundred times from its original value.

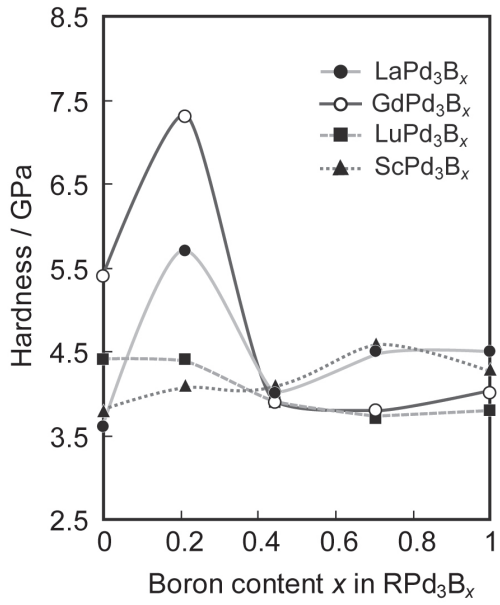

Fig.5 Vickers microhardness for RRh_3B_x.

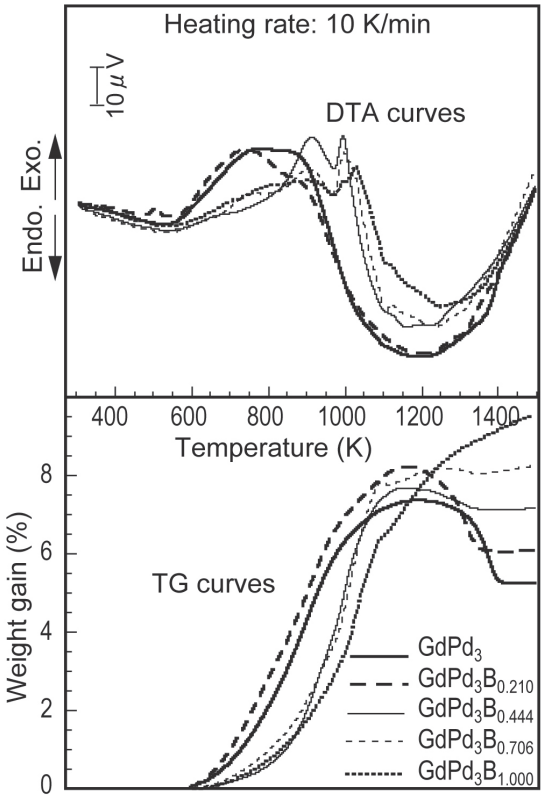

Fig.6 TG-DTA curves in the heating cycle for $GdRh_3B_x$.

4. Conclusions

Polycrystalline samples of RPd_3B_x (R = La, Gd, Lu, Sc) were successfully synthesized by the arc melting method and the

Table 1 Results of TG-DTA measurements on $GdPd_3B_x$.

TG-DTA	Oxidation onset (K)	Weight gain at 1473 K (%)	Weight gain (maximum)	Exotherm maximum (K)	Oxidized products
$GdPd_3$	590	5.3	7.5 % (1182 K)	771	Pd, Gd_2O_3
$GdPd_3B_{0.210}$	593	6.1	8.2 % (1152 K)	734	Pd, $GdBO_3$, Gd_2O_3
$GdPd_3B_{0.444}$	641	7.2	7.8 % (1136 K)	907, 990	Pd, $GdBO_3$, Gd_2O_3
$GdPd_3B_{0.706}$	628	8.3	-	896, 992	Pd, $GdBO_3$, Gd_2O_3
$GdPd_3B_{1.000}$	646	9.6	-	1022	Pd, $GdBO_3$

fundamental properties of the samples were investigated. The present study revealed the following conclusions.

1. The solid solution ranges of $GdPd_3B_x$, $LuPd_3B_x$ and $ScPd_3B_x$ are $0 \leq x \leq 0.45$, $0 \leq x \leq 0.5$ and $0 \leq x \leq 0.3$, respectively. In exceptional cases only, lattice shrinkage occurred with increasing x for $LaPd_3B_x$ in the range of $0 \leq x \leq 0.2$.
2. Temperature independent magnetic susceptibility was observed in RPd_3B (R = La, Lu, Sc) indicating Pauli paramagnetism. On the other hand, $GdPd_3B$ shows a paramagnetic behavior, which follows the Curie's law. The value of the effective Bohr magneton can be roughly evaluated as $p = 7.6$, which is consistent with the value of $p = 7.9$ of Gd^{3+} ions.
3. The Vickers microhardness for RPd_3B_x ranged over 3.5-7.5 GPa. In the cases of R = La and Gd, the hardness has a maximum in the vicinity of $x = 0.2$.
4. According to the DTA analysis, two exothermic peaks were observed at maximum temperatures of 907 K and 990 K for $GdPd_3B_{0.444}$. The increase in the weight due to oxidation was 7.8 %. The oxidized product was mixture of Pd, $GdBO_3$ and Gd_2O_3. Similar results are obtained for RPd_3B (R = La, Lu, Sc).

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